# Appendix 5-6: Annual Permit Compliance Monitoring Report for Mercury in the STAs

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# KEY FINDINGS AND OVERALL ASSESSMENT

This report summarizes data from compliance monitoring of mercury (Hg) storage, release, and biomagnification in Stormwater Treatment Areas (STAs). Fish data in this report are summarized for calendar year 2008 (CY2008) while surface water data are summarized for Water Year 2009 (WY2009) (May 1, 2008–April 30, 2009).

Key findings are as follows:

- 1. **All STAs:** There were no violations of the Florida Class III numerical water quality standard of 12 nanograms (ng) of total mercury per liter (THg/L) during the reporting year at any of the STAs. There were exceedances related to total mercury and methylmercury loading criterion as listed in the Protocol for Monitoring Mercury and Other Toxicants (SWFMD, 2006). These loading estimates are however highly uncertain due to a lack of data that resulted from a number of QA/QC failures. Aside from these exceedances, the project has met the action level requirements listed in the Protocol for Monitoring Mercury and Other Toxicants.
- 2. **STA-1W:** Stormwater Treatment Area 1 West (STA-1W) subsumed the Everglades Nutrient Removal (ENR) project in April 1999. The ENR project served as the prototype STA and had been in operation since 1994. After more than 10 years of operation, this STA maintained low concentrations of both total mercury (THg) and methylmercury (MeHg) in surface water. Methylmercury biomagnification in resident large-bodied fishes (e.g., sunfish and largemouth bass) has remained relatively constant over the monitoring period at levels almost an order of magnitude lower than observed in fishes from the downstream Everglades and the lowest with respect to all other STAs. Mercury levels in fish do not appear to pose a threat to fish-eating wildlife based on the U.S. Fish and Wildlife Service (USFWS) and the U.S. Environmental Protection Agency (USEPA) predator protection criteria.

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- 3. STA-1E: During WY2009, surface water THg and MeHg concentrations at the inflow and outflow locations were moderate compared to all other STAs, which is a contrast to previous water years. There were, however as with all other STAs, missed surface water data due to QA/QC failures. In recent years this STA showed some of the highest surface water THg levels in comparison to all other STAs and downstream monitoring locations, which may have been due to start-up related factors. For WY2009, THg and MeHg loading at the outflow was less than inflow. Mercury levels in mosquitofish (Gambusia holbrooki) from the interior marshes were the second lowest out of all STAs and did not change appreciably from the first to the fourth quarter of 2008. This again is a contrast from previous years where levels were on the high end. Mercury levels in sunfish (Lepomis spp.) and largemouth bass (Micropterus salmoides) were also on the low to moderate end as well. Regarding risks to fish-eating wildlife, mosquitofish (falling under trophic level 2 or 3) did not exceed the 77 nanograms per gram (ng/g) criterion. Nearly all resident sunfish of STA-1E were well below the USFWS criterion of 100 ng/g and the USEPA predator protection criterion of 77 ng/g for trophic level (TL) 3 fish. After whole-fish standardization, there was no exceedance of the USEPA criterion of 346 ng/g for TL 4 fish species for largemouth bass.
- 4. **STA-2:** For WY2009, both THg and MeHg remained at low concentrations in the outflow relative to previous years; however, inflow concentrations have increased two-fold since WY2006. For WY2009, outflow loading of MeHg was lower than inflow; however, outflow loading of THg was greater than inflow. The higher outflow loading for THg in STA-2 is likely related to the start-up of Cell 4 for in 2008. Average levels of mercury in mosquitofish have increased since 2007 (tissue-Hg; measured as ng Hg/g), but remain relatively low compared to all other STAs and downstream marshes. This increase in mosquitofish THg levels, including that for largemouth bass, has resulted in a parabolic trend which is likely related to the startup of Cell 4. This trend has since decreased to pre-startup conditions at both the interior and downstream locations. Sunfish from interior cells show no major change since 2007 but doubled at the downstream location. Regarding risk to fish-eating wildlife, all resident fish at STA-2 contained mercury levels less than both the USFWS and USEPA predator protection criteria for TL 3 species (100 ng/g and 77 ng/g, respectively). After whole-fish standardization, there was no exceedance of the USEPA criterion of 346 ng/g for TL 4 fish species for largemouth bass.
- 5. **STA-3/4:** In 2008, tissue-Hg levels in mosquitofish from this STA were low-moderate compared to mosquitofish from other STAs. In 2008, resident sunfish from the interior marshes of STA-3/4 contained moderate mercury levels compared to fish from all other STAs, but were lower in comparison to downstream sites. Mosquitofish contained mercury at concentrations lower than the criteria set by the USFWS (100 ng/g) and the USEPA (77 ng/g). Only one sunfish from the downstream location exceeded the USFWS criterion. THg concentration in largemouth bass from interior sites averaged 147 ng/g (± 13 ng/g), which is a 42 percent reduction from 2007. Overall, all fish species had shown a steady decrease since 2006. All largemouth bass from inflow, interior marshes, and outflow were less than the USEPA predator protection criteria based on TL 4 fish (346 ng/g).
- 6. **STA-5:** Water-column concentrations of both THg and MeHg remained low at the inflows and outflows of STA-5 during WY2009; however, data were available for only one quarter due to QA/QC failures. Outflow loading of MeHg from Flow-ways 1 and 2, was less than inflow for WY2009. Total mercury loading could not be calculated due to a lack of data from QA/QC failure. Mosquitofish and sunfish collected in 2008 contained mercury levels on the high end compared to other STAs. These high levels, particularly for mosquitofish, were largely the result of the startup of Flow-way 3. The lack of fish collection and the inability to age-standardize down through the years has made long-term evaluation of largemouth bass in this STA difficult. In 2008, largemouth bass within the interior marsh showed levels lower

- than expected [104 ng/g,  $\pm$  25 ng/g (non-age or length standardized)]. Fish-eating wildlife foraging preferentially from the interior marsh of STA-5 appears to be at low to moderate risk from mercury exposure and a slight elevated risk if feeding near site RA1.
- 7. STA-6: THg and MeHg concentrations at the inflows and outflows were similar throughout WY2009, and remained relatively low compared to previous spikes. All cells within STA-6 dried down twice during WY2009 for approximately three months. During and following the dryout periods neither THg nor MeHg spiked, yet surface water sulfate spiked multiple occasions up to four times beyond background levels. While it is possible that the methylation rate did not spike, past STA performance following the rewetting of the marsh indicates the likelihood that quarterly surface water mercury sampling missed a transient spike. For WY2009 MeHg outflow loading from STA-6 was less than inflow and outflow loading of THg was greater than inflow. These loadings estimated are however highly uncertain due to lack of data which results from quality assurance and quality control failures. During 2007, STA-6, Section 2, was put into operation. The start-up of Section 2 was the likely factor that caused a parabolic trend in THg concentration for mosquitofish and sunfish. Elevated levels in mosquitofish returned to pre-start-up conditions; however, elevated THg levels within sunfish still persist. A similar effect in mosquitofish and sunfish was seen for the start-up of cells/sections with in STA-2 and STA-5. Opposite from mosquitofish and sunfish, largemouth bass showed a 50 percent decrease from the previous years. Overall, this STA demonstrates some of the highest THg levels in all fish species. Despite lacking the observation of transitory spikes or constant elevated surface water MeHg concentrations (relative to other STAs), it is likely that the natural dry-out and re-flood process within this STA is playing a major role in the elevated THg levels in fish.

#### INTRODUCTION

This is the annual permit compliance monitoring report for mercury (Hg) in Stormwater Treatment Areas (STAs) by the South Florida Water Management District (SFWMD or District). The report summarizes the mercury-related reporting requirements of the Florida Department of Environmental Protection (FDEP) Everglades Forever Act (EFA) permits [Chapter 373.4592, Florida Statutes (F.S.)], including permits for STA-1W, STA-1E, STA-2, STA-3/4, STA-5, and STA-6. This report summarizes the results of monitoring in the calendar year 2008 (CY2008) for fish and Water Year 2009 (WY2009) (May 1, 2008–April 30, 2009) for surface water. The results of mercury monitoring at far-field sites downstream of the STAs in accordance with these permits, as well as non-Everglades Construction Project (non-ECP/EFA) discharge structures (Permit No. 06.502590709), is reported separately in Appendix 3B-1.

This report consists of key findings and overall assessment, an introduction and background, a summary of the Mercury Monitoring and Reporting Program, and monitoring results. The background section briefly summarizes previously identified and published concerns regarding possible impact of STA operations on South Florida's mercury problem. The subsequent section summarizes sampling and reporting requirements of the Mercury Monitoring Program within the STAs, followed by a summary and discussion of monitoring results. The discussion is divided into two subsections: (1) results from pre-operational monitoring and (2) results from STA operational monitoring during the reporting year, which comprises the bulk of the new discussion.

# **BACKGROUND**

Stormwater Treatment Areas are constructed wetlands designed to remove phosphorus from stormwater runoff originating from upstream agricultural areas and other areas, including Lake Okeechobee releases. The original six STAs—totaling about 50,000 acres—were built as part of the Everglades Construction Project (ECP/EFA) authorized under the EFA (Chapter 373.4592, F.S.).

Even prior to passage of the EFA, concerns were being raised that, in attempting to reduce downstream eutrophication, the restoration effort could inadvertently aggravate the mercury problem known to be present in the Everglades (Ware et al., 1990; Mercury Technical Committee, 1991). These concerns stemmed from studies in other areas that showed flooded soils in new impoundments to be a source of inorganic mercury (Cox et al., 1979). Of greater concern, studies also showed wetlands to be a significant site of mercury methylation.

Methylmercury (MeHg) is more bioaccumulative and toxic than the inorganic or elemental form of mercury (St. Louis et al., 1994; Rudd, 1995). Decomposition of flooded terrestrial vegetation and soil carbon in new reservoirs was reported to stimulate the sulfate-reducing bacteria that methylate inorganic mercury (Kelly et al., 1997; Paterson et al., 1998). Environments that favor methylation also drive bioaccumulation. For example, Paterson et al. (1998) found that annual fluxes of MeHg increased 10 to 100 times through a zooplankton community after impoundment.

Newly created reservoirs were also found to contain fish with elevated mercury burdens (Abernathy and Cumbie, 1977; Bodaly et al., 1984; Bodaly et al., 1999). This so-called "reservoir effect" can occasionally persist for several decades after initial soil flooding (Bodaly et al., 1984; Verdon et al., 1991; Fink et al., 1999). For instance, Verdon et al. (1991) reported that mercury levels in northern pike (*Esox lucius*) increased from 0.61 to 2.99 parts per million (ppm or mg/L) and continued to increase nine years after the initial soil flooding. Given these observations, Kelly et al. (1997) recently recommended that in siting a new reservoir (1) total land area flooded

should be minimized, and (2) flooding the wetlands, which contain more organic carbon than the uplands, should be avoided.

However, applying these observations directly to the Everglades is problematic because most of these observations were made in deepwater lakes or reservoirs in temperate regions. In a report to the SFWMD on the potential impact of nutrient removal on the Everglades nutrient problem (Watras, 1993), the author stated that "the boreal and temperate watersheds, wetlands and reservoirs studied to date are very different geologically, hydrologically, meteorologically and ecologically from the subtropical systems in the Everglades." Watras recommended monitoring and integrating mass balance and process-oriented studies to understand how this subtropical system would behave. Such studies were initiated in 1994 with the start-up of the prototype STA, the Everglades Nutrient Removal (ENR) Project. Baseline collections at the ENR Project (funded by the SFWMD and others) found no evidence of MeHg spikes in either surface water (PTI, 1994 attributed to KBN, 1994a; Watras, 1993 and 1994) or resident fishes [mosquitofish (*Gambusia holbrooki*) and largemouth bass (*Micropterus salmoides*); PTI, 1994 attributed to KBN, 1994b].

During the first two years of operation, median concentrations of total mercury (THg) and MeHg in unfiltered surface water were reported to be 0.81 and 0.074 nanograms per liter (ng/L), respectively (Miles and Fink, 1998). These low levels persisted in later years: from January 1998 through April 1999, median water-column concentrations in the interior marsh (i.e., excluding inflows and outflows) were 0.81 ng THg/L and 0.04 ng MeHg/L (Rumbold and Fink, 2002b).

Resident fishes also continued to have only low mercury levels: 8-75 nanograms per gram (ng/g) in mosquitofish, and 100-172 ng/g in three-year-old bass (Miles and Fink, 1998; SFWMD, 1999a; Lange et al., 1999). Finally, a mass balance assessment found the ENR Project to be a net sink for both THg and MeHg, removing approximately 70 percent of the inflow mass (Miles and Fink, 1998). Nonetheless, to provide continuing assurance that EFA implementation does not exacerbate the mercury problem, the FDEP construction and operating permits issued for the STAs require the SFWMD to monitor levels of THg and MeHg in various abiotic (e.g., water and sediment) and biotic (e.g., fish and bird tissues) media, both within STAs and the downstream receiving waters.

Results from monitoring programs at STAs constructed and operated since 1999 (after the ENR Project) have revealed transitory spikes in MeHg production (see previous reports published by the SFWMD, including Rumbold and Fink, 2002b). Combined with the results of a 1999 field study on the effect that drought and muck fires had on mercury cycling in the Everglades (Krabbenhoft and Fink, 2001), these monitoring results demonstrated that spikes can sometimes occur following dry-out and rewetting. Accumulating evidence suggests that oxidation of sulfide pools in the sediments (e.g., organic sulfide, disulfides, and acid volatile sulfides) during the dry-out can lead to increased methylation upon rewetting of the marsh either by providing free sulfate, which stimulates the sulfate-reducing bacteria or, in highly sulfidic areas, by reducing porewater sulfide, which can inhibit methylation (Benoit et al., 1999a and b).

# SUMMARY OF THE MERCURY MONITORING AND ASSESSMENT PROGRAM

The following section provides information on current monitoring and reporting activities used for the District's Mercury Monitoring and Assessment Program (MMAP) (SFWMD, 1999c). The MMAP was a plan developed for the Everglades Construction Project, the Central and Southern Florida Project, and the Everglades Protection Area (EPA). The SFWMD submitted this plan to the FDEP, the U.S. Environmental Protection Agency (USEPA), and the U.S. Army Corps of Engineers (USACE) in compliance with the permit requirements (SFWMD, 1999b).

Details on the procedures for ensuring the quality of and accountability for data generated in this monitoring program are set forth in the SFWMD's Quality Assurance Project Plan (QAPP) for the Mercury Monitoring and Assessment Program (SFWMD, 1999c), which was approved on issuance of the permit by the FDEP. QAPP revisions were approved by the FDEP on June 7, 1999.

On February 13, 2006, a revised sampling protocol was approved by both the FDEP and the District entitled A Protocol for Monitoring Mercury and Other Toxicants (Protocol) (SFWMD, 2006). Adapted from Rumbold and Pfeuffer (2005), this new plan was developed to replace the MMAP.

The primary drivers of the Protocol are to (1) stream-line sampling procedures; (2) eliminate the need for extended, open-ended sampling activities; and (3) phase-out surface water sampling. The same QAPP is used. As of May 16, 2008, all mercury monitoring within each STA follows the Protocol.

#### MERCURY MONITORING PROGRAM

#### **Everglades Mercury Baseline Monitoring and Reporting Requirements**

Levels of THg and MeHg in the pre-operational soils of each STA, and various abiotic and biotic media of the downstream receiving waters, define the baseline condition from which to evaluate mercury-related changes, if any, brought about by STA operations. The Everglades Mercury Background Report, prepared prior to the operation of the first STA, defines pre-EFA mercury baseline conditions (FTN Associates, 1999).

# **Pre-Operational Monitoring and Reporting Requirements**

Prior to the completion of construction and flooding of the soils for each STA, the District is required to collect 10-centimeter (cm) core samples of soil at six representative interior sites for THg and MeHg analyses. Prior to the initiation of discharge, the District is also required to collect biweekly samples of supply canal and interior unfiltered water for THg and MeHg analyses. If concentrations at the interior sites are not significantly greater than that of the supply canal, this information is reported to the permit-issuing authority, and then the biweekly sampling can be discontinued.

Discharge begins after all the start-up criteria are met. Results from pre-operational monitoring of STAs 1West, 1 East, 2, 3/4, 5, and 6 were reported previously (SFWMD, 1998c and 1999d; Rumbold and Rawlik, 2000; Rumbold and Fink, 2002a and 2003a; Rumbold, 2004 and 2005a; Rumbold et al., 2001 and 2006). **Figure 1** in this appendix summarizes the results of pre-operational sediment collection.

#### **Operational Monitoring**

Following approval for initiation of routine operation of an STA and thereafter, the EFA permits require that the following samples be collected at the specified frequencies and analyzed for specified analytes:

#### Water

On a quarterly basis, 500-milliliter unfiltered grab samples of water are collected in pre-cleaned bottles using the ultraclean technique at the supply canals and outflows of each STA 0.5 m below the water surface. They are analyzed for MeHg and THg (this includes the sum of all mercury species in a sample, including Hg<sup>0</sup>, Hg<sup>1+</sup>, and Hg<sup>2+</sup>, as well as organic mercury). THg results are analyzed for compliance with the Florida Class III water quality standard of 12 ng/L. Outflow concentrations of both THg and MeHg are compared to concentrations at the supply canal.

#### Sediment

Triennially, sediment cores are collected at depth from 0 to 10 cm at six representative interior sites. Each depth-homogenized core is then analyzed for THg and MeHg.

#### Prey Fish

Semiannually, grab samples in the range of 100 and 250 mosquitofish (*Gambusia* sp.) are collected using a dip net at the supply canal sites, interior sites, and outflow sites of each STA. Individual fish are composited from each size, the homogenate is subsampled in quintuplicate, and each subsample is then analyzed for THg. On March 5, 2002, the FDEP approved a reduction in the number of replicate analyses of the homogenate from five to three (correspondence from F. Nearhoof, FDEP). In 2007, reducing the homogenate from three to one was approved.

#### Top Predator Fish

Annually, 20 largemouth bass (LMB) (*Micropterus salmoides*) are collected primarily through electroshocking methods at representative supply and discharge canal sites and representative interior sites in each STA. Fish muscle (fillet) samples are analyzed for THg as an indicator of potential human exposure to mercury.

In 2000, the District began routine collection of sunfish (*Lepomis* spp.) at the same frequency, intensity (i.e., n = 20), and locations as for largemouth bass collection. This permit revision fulfilled a USFWS recommendation (USFWS recommendation 9b in USACE Permit No. 199404532; correspondence to Bob Barron, USACE, July 13, 2000). Sunfish, which are analyzed as whole fish, also serve as a surrogate for attempts to monitor mercury in wading birds that do not nest in the STAs. (For details on the monitoring program tracking mercury in wading birds in downstream areas see Appendix 3B-1.) The addition of sunfish to the compliance monitoring program was approved by the FDEP on March 5, 2002 (correspondence from F. Nearhoof, FDEP).

Tissue concentrations in each of the three monitored fishes reflect ambient MeHg levels, indicating their exposure as a function of factors including body size, age, rate of population turnover, and trophic position. Mosquitofish usually respond rapidly to changing ambient MeHg concentrations due to their small size, lower trophic status, short life span, and rapid population turnover. Mosquitofish become sexually mature in approximately three weeks and have an average lifespan of only four to five months; the lifespan of males is shorter than females (Haake and Dean, 1983; Haynes and Cashner, 1995; Cabral and Marques, 1999).

Conversely, the longer lifespan of sunfish (thought to have an average lifespan of four to seven years in the wild) and LMB means they ordinarily take longer to respond, in terms of tissue concentrations, to changes in ambient MeHg availability. Most importantly, sunfish and LMB represent exposure at higher trophic levels (TL) with a requisite time lag for trophic exchange. While this focus on a three-year old LMB is appropriate to evaluate exposure to fishermen, it complicates the data results by only interpreting tissue concentration over a three-year period. The key is to use these species-related differences to better assess MeHg availability within the system overall.

It is important to also recognize that virtually all of the mercury in fish muscle tissues (more than 85 percent) is in the methylated form (Grieb et al., 1990; Bloom, 1992). Therefore, the analysis of fish tissue for THg, which is a more straightforward and less costly procedure than for MeHg, can be interpreted as being equivalent to the analysis of MeHg. Further details regarding rationales for sampling scheme, procedures, and data reporting requirements are presented in SWFMD (1999).

# PROTOCOL FOR MONITORING MERCURY AND OTHER TOXICANTS

#### Phase 1: Baseline Collection and Assessment

Phase 1 baseline collection and assessment is meant to provide information regarding the likelihood that a constructed facility under an EFA project may exacerbate or create a mercury (or other toxicant) problem. Identifying problematic areas will allow managers to avoid sites or areas that may present risk.

Phase 1 is operated under three tier levels: Tier 1 (Compilation and Review of Available Data), Tier 2 (Field Sampling), and Tier 3 (Bioaccumulation Tests and Dynamic Modeling).

Under Tier 1, the Environmental Site Assessment (ESA) is evaluated to determine (1) if any corrective actions were taken during the ESA, (2) there was potential for contamination, and/or (3) the time interval between the ESA and project construction. If information data gaps exist, or where preponderance of the baseline data demonstrates a potential problem, then Phase 1, Tier 2, or Tier 3 is initiated.

Under Phase 1, Tier 2, five representative soil/sediment cores are collected and analyzed for several constituents that help evaluate MeHg production and mercury bioaccumulation. **Figure 1** summarizes sediment collection under Phase 1. Along with sediment, mosquitofish and large-bodied fish (sunfish, largemouth bass) are collected and analyzed for THg within the same operating unit (OU). The methods used for fish and sediment collection are described in the sections below.

Phase 1, Tier 3 is initiated if at least one of the following occurs: (1) absolute concentrations of MeHg or average percent MeHg in sediments/soils from an OU exceeds the 90 percent upper confidence level of the basin average or, if not available, the 75<sup>th</sup> percentile concentration (percent MeHg) for all basins; or (2) ambient fish collected with the project boundary demonstrate excessive bioaccumulation that exceeds the 90 percent upper confidence level of the basin-wide average or, if that value is not available, the 75<sup>th</sup> percentile concentration for all basins. Phase 1, Tier 3 is used to evaluate extending uncertainties surrounding mercury bioaccumulation. This is accomplished through the use of bioaccumulation testing and modeling.

# Phase 2: Monitoring During Three-Year Stabilization Period

If Phase 1 monitoring is not necessary, then Phase 2, Tier 2 monitoring can occur following OU flow-through. Under Phase 2, Tier 1, one surface water sample is collected and analyzed for THg and MeHg on a quarterly basis at inflow and outflow structures. Additionally, at least 100 mosquitofish are collected from multiple locations within each OU on a quarterly basis, to be composited and analyzed for THg. Sunfish and LMB ( $n \ge 5$ ) are collected and analyzed for THg on an annual basis.

Six criteria are used to evaluate the performance of an OU with respect to mercury bioaccumulation and enhancement (SFWMD, 2006). These criteria are related to long-term trends in fish tissue concentrations, surface water THg/MeHg loading, and water quality standards.

If any of the action criteria is exceeded, then Phase 2, Tier 2 is triggered. Tier 2 sequentially involves (1) notifying the permitting authority; (2) resampling the media that triggered Tier 2 Monitoring; (3) evaluating the spatial and temporal extent of the mercury bioaccumulation/enhancement accompanied with bioaccumulation modeling; and (4) developing an adaptive management plan.

# **Phase 3: Operational Monitoring**

If after the first three years of monitoring, neither downstream loading nor residue levels in fish have exceeded action levels in the two years prior, then the project can move into Phase 3, Tier 1. Under Phase 3, Tier 1, (1) surface water sampling is discontinued; (2) the frequency of mosquitofish collection is reduced to semiannually; and (3) the frequency of large-bodied fish collection is reduced to one collection event every three years. If the conditions are not met within the first three years, then criteria can be reevaluated annually based on the preceding two-year period.

Phase 3 Tier 2 is triggered if (1) the annual average THg levels in mosquitofish progressively increase over time; (2) any semiannual mosquitofish composite exceeds the 90 percent upper confidence level of the basin-wide annual average (or, if basin-specific data are lacking, it exceeds the 75<sup>th</sup> percentile concentration for the period of record for all basins); or (3) if triennial monitoring of large-bodied fish (i.e., in years 6 to 9) reveal tissue mercury levels have statistically increased over time (i.e., over two or more years) or have become elevated to the point of exceeding the 90 percent upper confidence level of the basin-wide annual average (or if basin-specific data are lacking, exceeds the 75<sup>th</sup> percentile for the period of record for all basins).

If fish under Phase 3 operational monitoring have not exceeded action levels by the ninth year, project-specific mercury monitoring can be moved into Phase 3, Tier 3. Under Phase 3, Tier 3, all of the project's mercury-related monitoring is discontinued; however, project managers are cautioned that action levels may be revised in the future.

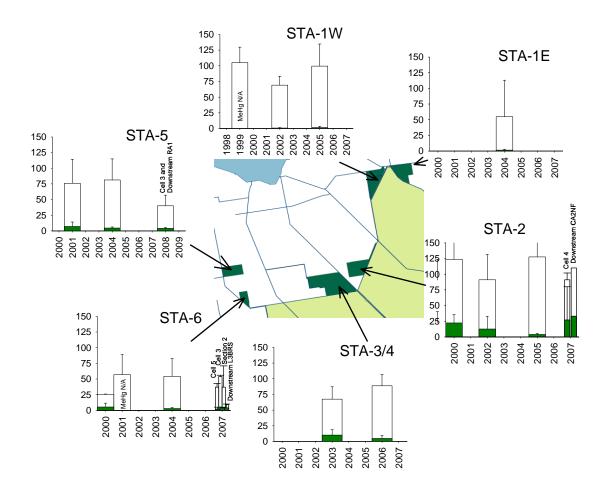


Figure 1. Mean concentration [+1 standard deviation (SD); dry-weight basis] of total mercury (THg) in nanograms per gram (ng/g) and methylmercury MeHg (10X ng/g) in sediment cores (n = 5 per cell/section; 0-10 cm) collected from each Stormwater Treatment Area (STA) to start-up. Crossed-hatched columns indicate collections following the new mercury monitoring program (SFWMD, 2006).

#### QUALITY ASSURANCE MEASURES

This section is a quality assessment of the District's mercury monitoring program during WY2009 and an evaluation of the accuracy, precision, and completeness of the data quality where appropriate. This assessment is based on data quality objectives contained in the QAPP.

Quality assurance and quality control (QA/QC) are integral parts of all monitoring programs. A stringent QA/QC program is especially critical when dealing with ultra-trace concentrations of analytes in natural and human-impacted environments. Quality assurance includes design, planning, and management activities conducted prior to implementing the project to ensure that the appropriate types and quantities of data will be collected with the required representativeness, accuracy, precision, reliability, and completeness. The goals of QA are to ensure the following: (1) standard collection, processing, and analysis techniques will be applied consistently and correctly; (2) the number of lost, damaged, and uncollected samples will be minimized; (3) the integrity of the data will be maintained and documented from sample collection to entry into the data record; and (4) data are usable based on project objectives.

Quality assurance measures are incorporated during the sample collection and laboratory analysis to evaluate the quality of the data. These measures give an indication of measurement error and bias (or accuracy and precision). Aside from using these results as an indication of data quality, an effective QA program must utilize these QC results to determine areas of improvement and implement corrective measures. QC measures include both internal and external checks. Typical internal QC checks include replicate measurements, internal test samples, method validation, blanks, and the use of standard reference materials. Typical external QC checks include split and blind studies, independent performance audits, and periodic proficiency examinations. Data comparability is a primary concern because mercury-related degradation of water quality is defined here as relative to baseline data generated by one or more laboratories. It is important to establish and maintain comparability of the performance and results among participating laboratories assessing the reporting units and calculations, database management processes, and interpretative procedures. Comparability of laboratory performance must be ensured if the overall goals of the monitoring program are to be realized.

#### **Laboratory Quality Control**

Data for this program was generated by the District and the FDEP, both of which are certified by the Florida Department of Health under the National Environmental Laboratory Accreditation Program. The following methods were utilized when analyzing samples for THg and MeHg during WY2009: FDEP–USEPA Method 1631E (Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry); USEPA Draft Method 1630 (Methylmercury in Water and Tissues by Distillation, Extraction, Aqueous Phase Ethylation, Purge and Trap, Isothermal GC Separation, Cold Vapor Atomic Fluorescence Spectrometry); USEPA Method 245.6 [Mercury in Tissues by Cold Vapor AAS (uses liquid digestion)]; EPA 7471A [Mercury in solids by Cold Vapor AAS (uses liquid digestion)]; District–EPA 7473 [Mercury in solids and tissues by direct thermal decomposition, amalgamation and AA (does not incorporate liquid digestion)]. All of the above methods use performance-based standards employing the appropriate levels of QA/QC required by National Environmental Laboratory Accreditation Conference, the specific reference method, and the Protocol.

#### Field Quality Control Samples

A total of 48 field QC samples, including field kit prep blanks (FKPB), equipment blanks [both laboratory-cleaned equipment blanks (EB) and field-cleaned equipment blanks (FCEB)], and replicate samples (RS) were collected for both THg and MeHg surface water samples at STA-1W, STA-1E, STA-2, STA-3/4, STA-5, STA-6, and non-EFA structures (project code

HGLE) during WY2009. These field QC check samples represented approximately 38 percent of the 125 water samples collected during this reporting period. The results of the field QC blanks are summarized in **Table 1**. An FKPB is a sample of the deionized distilled water (DDW) sent as blank water for field QC that remains at the lab to monitor low-level background inorganic mercury contamination of the laboratory DDW system, which can vary over time. An EB is collected at the beginning of every sampling event, and an FCEB is collected at the end of the event. Quality control results for this water year were significantly different than WY2008. The percent of flagged samples doubled for THg in EB and FCEB. For WY2007, WY2008, and WY2009, the greatest percentages of '% Flagged' were for EB.

**Table 1.** Frequency of field quality control (QC) blanks from STAs 1 West, 1 East, 2, 3/4, 5, and 6, and non-Everglades Forever Act (non-EFA) structures/area surface water samples. Detection limits are 0.1 ng THg/L and 0.022 ng MeHg/L.

THg						MeHg						
FieldQC <sup>1</sup>	n <sup>2</sup>	Collection <sup>4</sup> Frequency %	n > MDL <sup>5</sup>	Mean ng/L <sup>3</sup>	n Flagged	% Flagged	n²	Collection <sup>4</sup> Frequency %	n > MDL <sup>5</sup>	Mean ng/L <sup>3</sup>	n Flagged	% Flagged
FKPB	1	2.0	0	-	0	0	1	2.0	0	0	0	0
EB	3	12.0	1	0.43	1	33.0	5	20.0	0	-0.022	0	0
FCEB	10	40.0	3	0.10	1	10.0	8	32.0	0	-0.022	0	0

<sup>&</sup>lt;sup>1</sup>FKPB-Field kit preparation blank, EB-Lab-cleaned equipment blank, FCEB-Field-cleaned equipment blank collected at the end of the sampling event.

# **Analytical and Field Sampling Precision**

Field replicates are samples that have been collected in rapid succession from the same site. Laboratory replicates are aliquots of the same sample that are prepared and analyzed within the same run. On May 18, 2009, the sample corrective action criteria for FCEB and EBs was raised from 3x to 10x the FCEB/EB level. Raising this level flags all routine samples associated with an FCEB or EB if its value is less than 10x the method detection limit of 0.1 ng/L for THg or 0.022 ng/L for MeHg. This change in corrective action was implemented due to an update in instrumentation from the primary analytical laboratory (FDEP).

# Water Samples

To assess the precision of field collection and analysis, 20 replicate, unfiltered surface water samples (10 THg and 10 MeHg) collected at STA-1W, STA-1E, STA-2, STA-3/4, STA-5, STA-6, and non-EFA structures were processed during the course of WY2009. **Table 2** reflects the results of the sample analyses. Two replicate samples (RS) were matched with one surface water sample. For WY2009, all but one of the THg relative standard deviations were above the required 20 percent QA/QC precision level. None of the MeHg relative standard deviations were above the 20 percent QA/QC precision level.

<sup>&</sup>lt;sup>2</sup>Total number (n) of surface water samples collected from these structures/sites during WY2009 was 25 THg and 25 MeHg.

<sup>&</sup>lt;sup>3</sup>Mean concentration of quality control (QC) samples.

 $<sup>^{4}</sup>$ Percentage of all samples collected (n = 25 for THg and n = 25 for MeHg).

<sup>&</sup>lt;sup>5</sup>MDL-Method detection limit

#### Mosquitofish Composite Samples

To monitor spatial and temporal patterns in mercury residues in small-bodied fish, mosquitofish (100 to 250 individuals) were collected at various locations in the STAs, EFA, and non-EFA marshes. These individuals were then composited for each site. Composite sampling can increase sensitivity by increasing the amount of material available for analysis, reduce inter-sample variance effects, and dramatically reduce analytical costs. However, there are disadvantages to composite sampling. Subsampling from a composite introduces uncertainty if homogenization is incomplete. Since 1999, the District has used a Polytron® homogenizer to homogenate composited mosquitofish. Until late 2001, the homogenate was sub-sampled in quintuplicate and each sub-sample analyzed for THg. Based on the apparent degree of homogenization as evidenced by the low relative standard deviation (RSD) among aliquots reported in the 2002 Everglades Consolidated Report, the District revised its Standard Operation Procedure after consultation with and approval by the FDEP, reducing subsampling of the homogenate from five to three. In 2007, replicates were further reduced from three to one homogenate. Laboratory replicates of mosquitofish were processed by SFWMD and analyzed for THg. For CY2008, the mean percent RSD between replicate and routine samples for the 33 aliquots was 9.0 percent (**Table 2**) which is similar to CY2007 (mean of 9.6 percent). None of the RSDs were greater than the required 20 percent QA/QC precision level.

#### Sediment Composite Samples

For CY2008, a total of two replicate sediment samples were collected for THg and MeHg analysis (two replicates each for THg and MeHg) across all STA and downstream monitoring projects. These samples were collected from STA-5 (project ST5D). The routine sediment THg value was 0.026 milligrams per kilogram (mg/kg) and MeHg was 0.00048 mg/kg. Both RSDs were below the required 20 percent QA/QC precision level (**Table 2**).

**Table 2.** Precision among replicate unfiltered surface water samples and mosquitofish and sediment collected at STA-1W, STA-1E, STA-2, STA-3/4, STA-5, STA-6, and non-EFA structures.

	% Relative Standard Deviation (RSD)*							
Analyte	n	Minimum	Maximum	Mean	Median			
<sup>†</sup> Surface Water THg	5	4.0	58	37	40			
<sup>†</sup> Surface Water MeHg	5	4.5	9.4	6.7	6.8			
<sup>‡</sup> Mosquitofish THg	11	5.0	15.4	9.0	7.5			
<sup>‡</sup> Sediment THg	1	14.0	§NA	<sup>§</sup> NA	§NA			
<sup>‡</sup> Sediment MeHg	1	7.5	§NA	§NA	<sup>§</sup> NA			

\* 
$$\left(\frac{SD}{Mean}\right) x 100$$

<sup>§</sup> Data unavailable due to only one RSD calculated

<sup>†</sup> Based on Water Year 2009 (WY2008) (May 1, 2008–April 30, 2009)

<sup>‡</sup> Based on calendar year 2008 (CY2008) (January 1, 2008–December 31, 2008)

#### Inter-laboratory Comparability Studies

To ensure further reproducibility between ongoing mercury sampling initiatives and to evaluate the performance of contract laboratories used for mercury analysis, round-robin studies for water, fish, and sediment are routinely initiated. These studies are done by the District and contracted laboratories.

#### Surface Water and Fish

As in previous years, in CY2008 an inter-laboratory study was initiated by the FDEP for the purpose of assessing the comparability of total and MeHg analysis in water for several laboratories. Participating laboratories received nine unknown samples of ambient water from the Everglades for analysis of THg and/or MeHg. See the attachment to Appendix 3B-1. The District did not participate in any fish THg inter-laboratory study during CY2008; however, in CY2009, the District will participate in a QUASIMEME study.

#### Sediment

In CY2008, the District participated in a performance testing (PT) study to assess the ability of the District's laboratory to generate acceptable analytical data for THg in sediment/soil. For details on this study see the attachment titled Soil/Hazardous Waste Proficiency Testing: *SOIL-62 Final Report* at the end of this appendix.

#### STATISTICAL METHODS

The proper interpretation of residue levels in tissues can sometimes prove problematic due to the confounding influences of age or species of collected animals. For comparison, special procedures are used to normalize the data (Wren and MacCrimmon, 1986; Hakanson, 1980). To be consistent with the reporting protocol used by the Florida Fish and Wildlife Conservation Commission (FWC) (Lange et al., 1998 and 1999), mercury concentrations in LMB were standardized to an expected mean concentration in three-year-old fish at a given site by regressing mercury against age (EHg3). Currently, the FWC targets LMB between a length of 280–330 millimeters (mm) which includes EHg3 fish. This length range is targeted to eliminate the need for fish ageing. Sunfish were not aged. Instead, arithmetic means were reported. Additionally, the distribution of the different species of sunfish (warmouth, *L. gulosus*; spotted sunfish, *L. punctatus*; bluegill, *L. macrochirus*; and redear sunfish, *L. microlophus*) that were collected during electroshocking was also qualitatively considered as a potential confounding influence on mercury concentrations prior to each comparison.

Where appropriate, analysis of covariance (ANCOVA) using the SAS General Linear Model procedure, was used to evaluate spatial and temporal differences in mercury concentrations, with age (LMB) or weight (sunfish) as a covariate. However, use of ANCOVA is predicated on several critical assumptions (Zar, 1996). These assumptions are that (1) regressions are simple linear functions; (2) regressions are statistically significant (i.e., nonzero slopes); (3) covariate is a random, fixed variable; (4) both the dependent variable and residuals are independent and normally distributed; and (5) slopes of regressions are homogeneous (parallel, i.e., no interactions). Regressions also require that collected samples exhibit a relatively wide range of covariate—that is, that fish from a given site are not all the same age or weight. Where these assumptions were not met, ANCOVA was inappropriate. Instead, standard analysis of variance [ANOVA (n > 2 groups)] or Student's t-tests ( $n \le 2$  groups) were used.

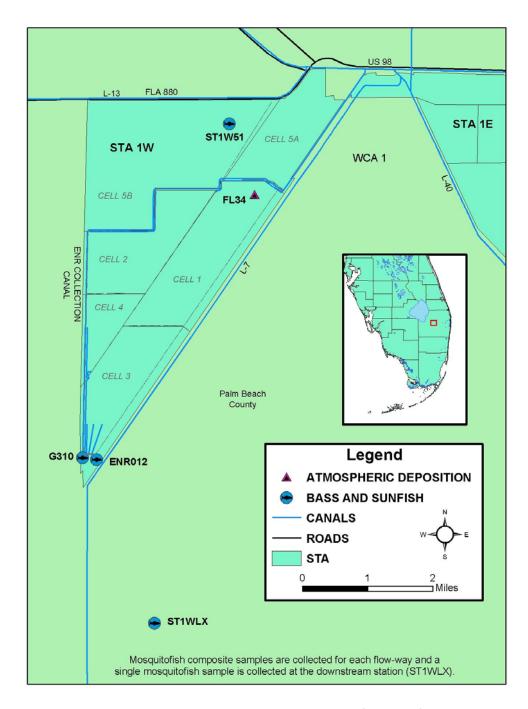
Possible covariates were considered separately and often qualitatively. The assumptions of normality and equal variance were tested by the Kolmorogov-Smirnov and Levene Median tests, respectively. Datasets that either lacked homogeneity of variance or departed from normal

distribution were natural-log transformed and reanalyzed. If transformed data met the assumptions, then they were used in ANOVA. If multi-group null hypotheses were rejected under ANOVA, then the group was compared using either Tukey HSD (Honestly Significant Difference; for equal-sized datasets) test, the Tukey-Kramer (for unequal-sized datasets), or the Holm-Sidak test.

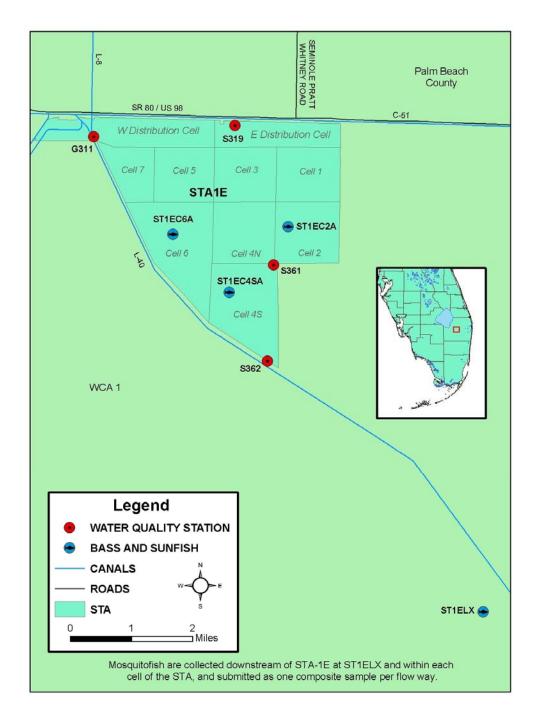
If the group did not meet any of these assumptions, then raw datasets were evaluated using nonparametric tests such as the Kruskal-Wallis ANOVA on ranks (n > 2 groups) or the Mann-Whitney Rank sum test ( $n \le 2$  groups). If the multi-group null hypothesis was rejected, then the groups were compared using either the Nemenyi test (for equal-sized datasets) or Dunn's Method (for unequal-sized datasets). The Pearson Product moment (or the non-parametric equivalent Spearman Rank Order) was used to evaluate the relationship between two parameters. Linear regression was used to develop a line of best fit (linear model) between parameters.

### SITE DESCRIPTIONS

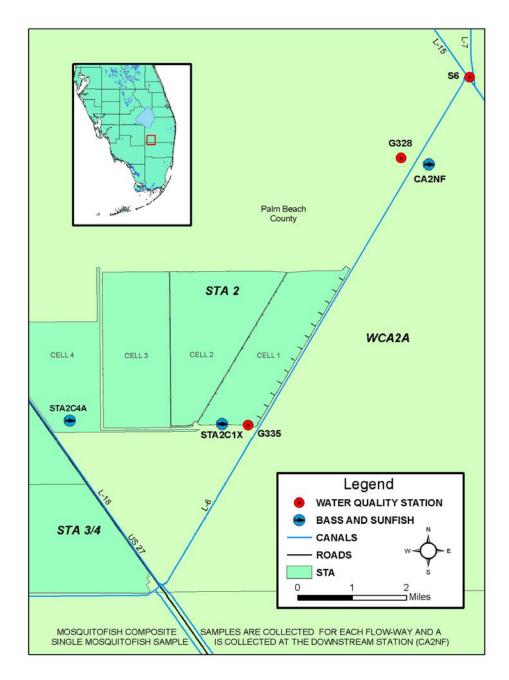
Site descriptions and operational plans for STA-1W, STA-1E, STA-2, STA-3/4, STA-5, and STA-6 are published elsewhere (SFWMD, 2007a-d; 2009). For maps of monitoring locations, see **Figures 2** through **7**.



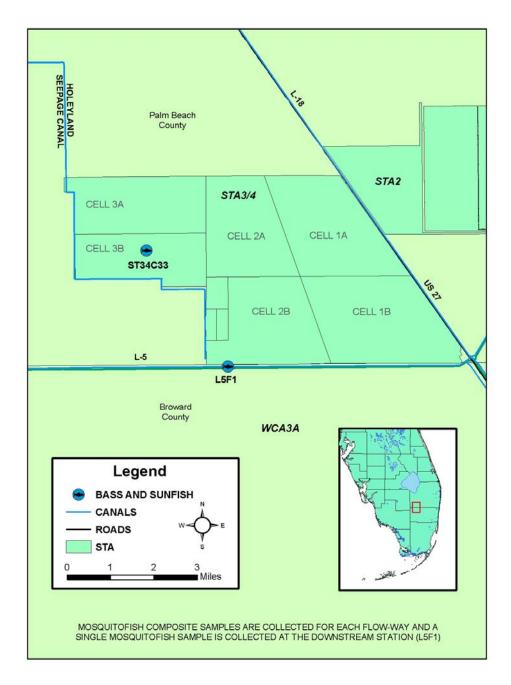
**Figure 2.** Stormwater Treatment Area 1 West (STA-1W) showing current mercury monitoring sites.



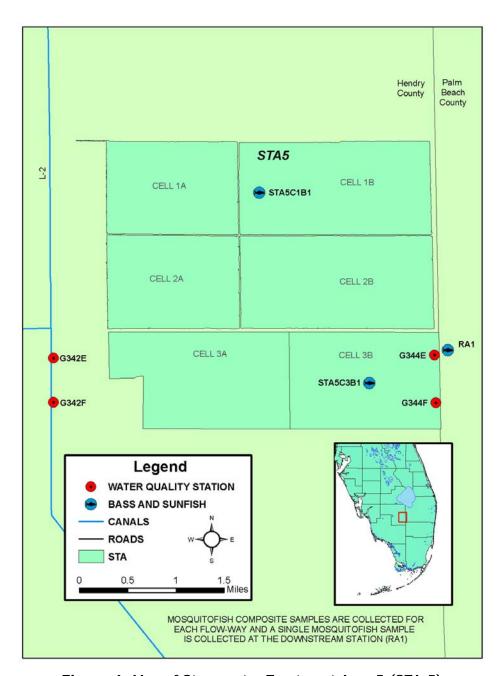
**Figure 3.** Map of Stormwater Treatment Area 1 East (STA-1E) showing current mercury monitoring sites.



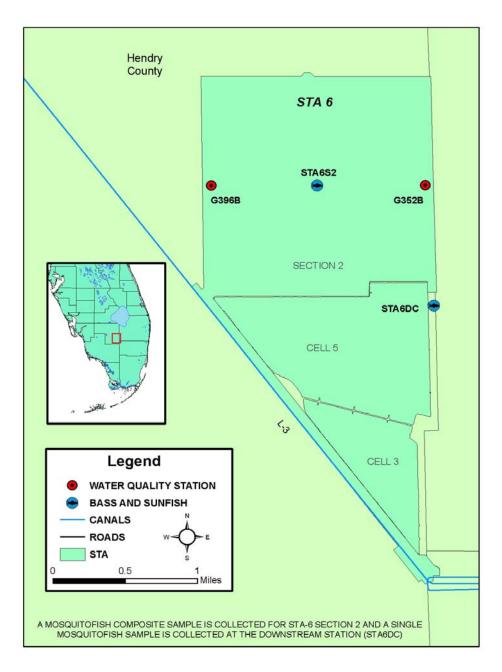
**Figure 4.** Map of Stormwater Treatment Area 2 (STA-2) showing current mercury monitoring sites.



**Figure 5.** Map of Stormwater Treatment Area 3/4 (STA-3/4) showing current mercury monitoring sites.



**Figure 6.** Map of Stormwater Treatment Area 5 (STA-5) showing current mercury monitoring sites.



**Figure 7.** Map of Stormwater Treatment Area (STA-6) showing current mercury monitoring sites.

#### MONITORING RESULTS

# STA-1W

In 2000, STA-1W subsumed the ENR Project (Cells 1 through 4, **Figure 2**), which had been in operation since 1994. STA-1W surface water passed start-up criteria during the week of January 17, 2000; flow-through operations began in early February 2000. Formal monitoring of mercury levels in STA-1W surface water began on February 16, 2000 (for discussion of results observed prior to WY2009, see Rumbold and Rawlik, 2000; Rumbold et al., 2001, 2006; Rumbold and Fink, 2002a, 2003a; Rumbold, 2004, 2005a, Gabriel et al., 2007). In 2007, all mercury monitoring was moved into Phase 3-Operational Monitoring (SFWMD, 2006). Thus, surface water monitoring for THg and MeHg was terminated. The last surface water data was collected in August of 2007. Information on THg and MeHg for STA-1W is presented in previous SFERs.

Concentrations of THg in mosquitofish in CY2008 are summarized in Table 3 and graphically presented in Figure 8. Mosquitofish from STA-1W continue to have very low mercury levels particularly from the interior sampling sites. These levels are similar to previous conditions when the area was operated as the ENR project (Rumbold and Fink, 2002b). Furthermore, mercury levels in STA-1W mosquitofish continue to be lower than levels currently observed in fish from other areas of the Everglades (see Appendix 3B-1). Mosquitofish in STA-1W have consistently exhibited a negative percent change in tissue mercury levels since this STA was put into operation (Table 3). The slope of this decreasing trend has in recent years reached closer to zero, likely indicating that the internal mercury biogeochemical cycle has reached a minimum in fish THg concentration. This pattern was also observed in sunfish and largemouth bass. In 2008, the outflow locations G310 and ENR012 were replaced with downstream location ST1WLX, resulting in overall higher levels as downstream marsh locations typically contain higher fish mercury concentrations. For CY2008, there were statistical spatial differences in mosquitofish concentration across all STAs (Kruskall-Wallis; p < 0.001; df = 5, H = 24). Total mercury concentration in mosquitofish from STA-1W, 2, and 3/4 were less than STA-6; STA-6 and STA-5 were not statistically different. The average annual total mercury mosquitofish composite concentration for CY2008, including all individual mosquitofish composites within STA-1W, did not exceed the period of record (POR) 75<sup>th</sup> percentile for all Southern Everglades downstream receiving water sampling locations (see Appendix 3B-1).

As shown in **Table 4** and **Figure 8**, STA-1W sunfish continue to have the lowest mercury levels than any other STA or downstream monitoring location (see Appendix 3B-1). Sunfish mercury levels can, however, vary depending upon several factors, namely, species type, size and age. After standardizing all sunfish by the most predominant type [bluegill (*Lepomis macrochirus*)] and normalizing by length, statistical differences existed among interior STA locations (Kruskall-Wallis; p < 0.001; df = 5, decomparises the statistical difference was between STA-1W and STA-6 (Dunn's Method of pair-wise comparisons). Bluegill for all other STAs was not statistically different. The average annual sunfish THg concentration for all locations within STA-1W did not exceed the POR 75<sup>th</sup> percentile for all Southern Everglades downstream receiving water sampling locations (see Appendix 3B-1) during 2008.

As with sunfish, largemouth bass from the interior sites of STA-1W contained mercury levels lower than bass from all other interior STA sites (**Table 5** and **Figure 8**). Moreover, STA-1W LMB contained much lower mercury than fish from downstream sites in the WCAs (see Appendix 3B-1). As with mosquitofish and sunfish, LMB exhibit an overall long-term negative percent change in mercury levels in STA-1W (**Table 5**). The average annual largemouth bass

THg concentration did not exceed the POR 75<sup>th</sup> percentile for all Southern Everglades downstream receiving water sampling locations (see Appendix 3B-1) during 2008.

All fish species from the interior cells (ST1W51, ENR302, ENR401, ENR012) from STA-1W show no visible temporal increase in THg for  $\geq 3$  years to merit statistical investigation. Prior to performing the above temporal trend analyses for this STA and all other STAs, sunfish standardized to only include the bluegill species and divided by length.

Mercury levels in fish tissue can also be evaluated for risk to fish-eating wildlife. Contrary to other areas of the Everglades, fish-eating wildlife foraging preferentially at STA-1W do not appear to be at risk from mercury exposure. STA-1W mosquitofish, sunfish, and LMB continue to have some of the lowest tissue-Hg levels in South Florida—well below both the USEPA and USFWS guidance level for predator protection (Eisler, 1987; USEPA, 1997). Therefore, fish-eating wildlife foraging preferentially at STA-1W appears to have an overall low risk to mercury exposure.

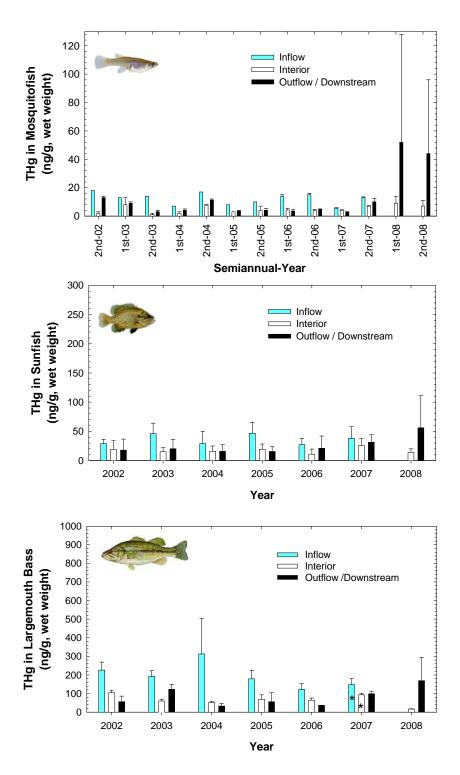
Water-column sulfate, stage, and rainfall at STA-1W are presented in Figure 9.

**Table 3.** Concentration of THg (ng/g, wet weight) in mosquitofish (*Gambusia holbrooki*) composites from STAs.

STA	Half-year/ Quarterly	Inflow Fish	Interior Fish	Outflow/Downstream Fish	Percent Change(%) <sup>a</sup>
	2008-1	Not Applicable	9.3	52.0	Not Applicable
CTA 410/	2008-2	Not Applicable	7.0	44.3	Not Applicable
STA-1W	Annual mean	Not Applicable	8.1	48.1	Not Applicable
	Cumulative mean	Not Applicable	19.3	14.6	Not Applicable
	2008-1	Not Applicable	15.3	94	Not Applicable
	2008-2	Not Applicable	16.3	81	Not Applicable
CTA 4F	2008-3	Not Applicable	15.3	74	Not Applicable
STA-1E	2008-4	Not Applicable 14.0		116	Not Applicable
	Annual mean	Not Applicable	15.2	91	Not Applicable
	Cumulative mean	Not Applicable	20.5	72.4	Not Applicable
	2008-1	Not Applicable	15.2	34.0	Not Applicable
	2008-2	Not Applicable	21.7	45.3	Not Applicable
CTA O	2008-3	Not Applicable	21.5	52.0	Not Applicable
STA-2	2008-4	Not Applicable	13.7	30.0	Not Applicable
	Annual mean	Not Applicable	18.0	40.3	Not Applicable
	Cumulative mean	Not Applicable	71.0	72.0	Not Applicable
	2008-1	16.6	15.0	23.7	30.0
STA-3/4 <sup>b</sup>	2008-2	Not Applicable	10.0	30.0	Not Applicable
51A-3/4	Annual mean	16.6	12.5	26.8	Not Applicable
	Cumulative mean	14.0	15.1	28.0	110
	2008-1	Not Applicable	24.3	28.0	Not Applicable
	2008-2	Not Applicable	35.3	24.5	Not Applicable
STA-5	2008-3	Not Applicable	33.3	62.0	Not Applicable
51A-5	2008-4	Not Applicable	19.3	21.3	Not Applicable
	Annual mean	Not Applicable	28.1	34.0	Not Applicable
	Cumulative mean	Not Applicable	25.5	30.6	Not Applicable
	2008-1	Not Applicable	25.0	41.0	Not Applicable
	2008-2	Not Applicable	54.3	45.0	Not Applicable
STA 6	2008-3	Not Applicable	56.0	116	Not Applicable
STA-6	2008-4	Not Applicable	19.0	49.0	Not Applicable
	Annual mean	Not Applicable	38.5	62.7	Not Applicable
	Cumulative mean	Not Applicable	16.2	25.3	Not Applicable

a Percent change = (outflow-inflow/inflow)\*100

b Overlap between new and old mercury monitoring plans



**Figure 8.** Mercury concentrations (ng/g, wet weight) in (*top*) mosquitofish composites (±SD), (*middle*) whole sunfish (*Lepomis* spp.) (±SD), and (*bottom*) fillets of largemouth bass (*Micropterus salmoides*) (arithmetic, SD) collected at STA-1W. An asterisk indicates an arithmetic mean of all available largemouth bass.

**Table 4.** Concentration of THg (ng/g, wet weight) in sunfish collected from STAs in 2007 (sample size in parentheses).

STA	Interior Fish	Outflow/Downstream Fish	
STA-1W	$14 \pm 6.5 (5)$	$56 \pm 55 (15^{a})$	
Cumulative mean	19.0	25.3	
STA-1E	$42 \pm 10 (15^{a})$	292 ± 15 (5)	
Cumulative mean	70	170	
STA-2	$49 \pm 25 (7^{a})$	171 ± 116(20 <sup>a</sup> )	
Cumulative mean	97	111	
STA-3/4	40 ± 12 (5)	$66 \pm 22 (5)$	
Cumulative mean	75	70	
STA-5	$66 \pm 20 (10^{a})$	$67 \pm 7 (6^{a})$	
Cumulative mean	97	92	
STA-6	102 ± 33 (5)	110 ± 29(5)	
Cumulative mean	56	93	

a Where n > 5, multiple sites were sampled and pooled, i.e., multiple interior or outflows (see the *Protocol for Monitoring Mercury and Other Toxicants* section of this appendix).

**Table 5.** Length-censored (280-330 millimeters) and cumulative (in parentheses) THg (ng/g, wet weight) concentration data in fillets from largemouth bass collected at STAs in 2008. All data show arithmetic mean  $\pm$  1 SD.

STA	Interior Fish	Outflow/Downstream Fish		
STA-1W	16 ± 2, 3 <sup>c</sup> (26 ± 15,5)	169 ±126, 7 <sup>a</sup> (142 ± 146,15 <sup>a</sup> )		
Cumulative mean	61	79		
STA-1E	$204 \pm 107, 6^{a}$ ) $(157 \pm 87, 15^{a})$	NA* (166, ± 84,5)		
Cumulative mean	192	322		
STA-2	$255 \pm 57, 3^{\circ}$ (258 ± 45, 5)	$307 \pm 201, 4^{\circ}$ (372 ± 167, 20 <sup>a</sup> )		
Cumulative mean	248	532		
STA-3/4	$147 \pm 13, 4^{c}$ (224 ± 172, 5)	262, 46, 2° (325 ± 76, 5)		
Cumulative mean	313	423		
STA-5	108,1° (104 ± 25, 5)	$210 \pm 107, 4^{c}$ (202 ± 94, 5)		
Cumulative mean	327	362		
STA-6	252,1° (226 ± 66, 5)	386±115, 3° (425 ± 109,5)		
Cumulative mean	201	471		

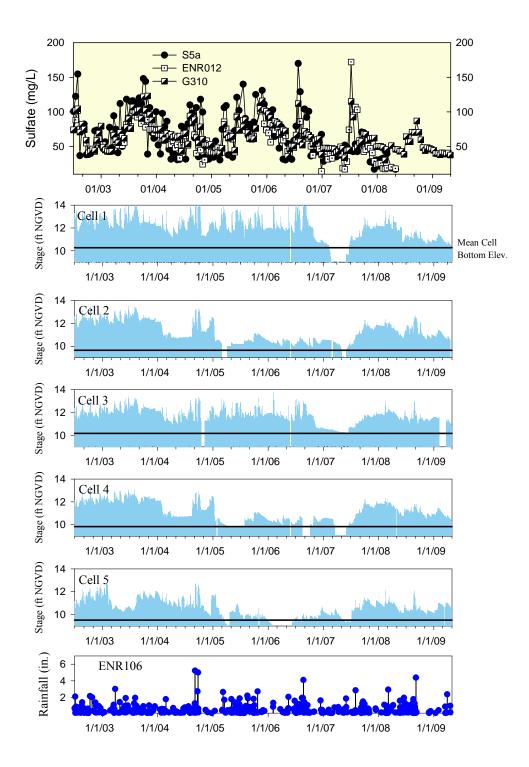
a Where n > 5; multiple sites were sampled and pooled, i.e., multiple interior or downstream/outflows (see the *Protocol for Monitoring Mercury and Other Toxicants* section of this appendix)

b Where  $n \le 5$ , not enough fish in sample area

c Where n < 5, not enough fish with the 280–330 millimeter (mm) length range

NA Not available; no fish in sample area

NA\* Not available; no fish within the sample length range (280-330 mm)



**Figure 9.** Water-column sulfate, stage (recorded immediately upstream of outflow culvert of cell), and rainfall at STA-1W.

#### STA-1E

Monitoring water-column concentrations of THg and MeHg began in January 2005 at STA-1E. Both the central flow-way (Cells 3, 4N, and 4S) and the westernmost flow-way (Cells 5–7) met the start-up criteria, as specified in EFA Permit No. 0195030-001-GL, in August 2005 (correspondence from R. Bearzotti, SFWMD, dated September 9, 2005). The USACE constructed a Periphyton-Based Stormwater Treatment Area (PSTA) Demonstration Project in the easternmost flow-way (Cells 1 and 2) of STA-1E. The most recent eastern flow-way passed startup in 2007. Currently, all of STA-1E is under Phase 2 monitoring.

In WY2009, STA-1E displayed moderate surface water THg concentrations in comparison to all other STAs (**Figures 10** and **11**). Inflow concentrations were comparable to most other STAs (**Figure 12**) which is a contrast to previous water years. MeHg remained at relatively low concentrations in the outflow locations (S-362 and S-361) following the operation of the central, western, and eastern flow-ways, and outflow concentrations were typically lower than inflow (**Figure 12**). Despite overall high THg, levels from this STA are below the WQS of 12 ng/L. The high THg levels may be related to several factors including: (1) construction issues during start-up operations, (2) high pre-existing soil mercury concentrations, (3) high mercury levels within source water discharging into this STA, and (4) "first-flush" effects. The elevated mercury levels are not related to impacts from dry-out and rewetting as each cell has been inundated since early 2006 (**Figure 13**). Similar to performance-related concentrations, both THg and MeHg loads at the outflow were marginally below inflow [206g THg (inflow), 46.4g MeHg (inflow); 145g THg (outflow), 27.4g MeHg (outflow)] (**Table 6**).

Quarterly collection of mosquitofish from STA-1E sites at interior marshes and the single downstream site (ST1ELX), began during the third quarter of 2005. As shown in **Table 3**, mercury levels in mosquitofish from the interior marsh were the second lowest with respect to all other STAs in 2008. This is a much different scenario in comparison to 2007 where mosquitofish levels were greater than all other STAs except STA-6. As with many STAs, levels were much higher in downstream locations than the interior sites (**Figure 14**). Average annual mosquitofish composites for the interior of STA-1E, including all mosquitofish composites, did not exceed the POR 75<sup>th</sup> percentile for all Southern Everglades downstream receiving water sampling locations (see Appendix 3B-1) during 2008.

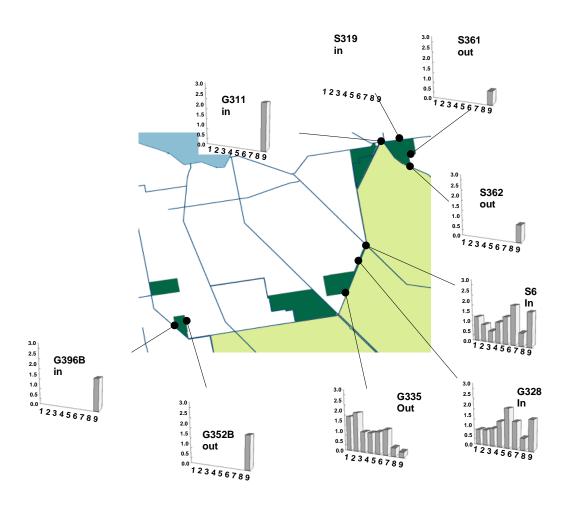
Annual collection of sunfish occurred in October 2008. As evident from **Table 2**, mercury levels were on the lower end in STA-1E sunfish compared to the other STAs. Levels in fish from the near-field downstream site (ST1ELX) were double the levels recently observed at one of the far-field downstream sites, LOX4 (see Appendix 3B-1). The standardized concentration in bluegill from ST1ELX was 1.4 ng/g/mm, whereas bluegill from nearby LOX4 averaged 0.76 ng/g/mm (**Figure 14**), which contrasts the previous two years where levels at both stations were similar.

For 2008, largemouth bass were collected from the STA-1E interior site and the downstream site (**Table 5**); however, no LMB between the 280–330 mm range were caught from the downstream site. Largemouth bass THg levels within the interior of STA-1E were similar in spatial pattern to sunfish, where concentrations were on the moderate end compared to all other STAs. The average annual LMB THg concentration for interior and downstream locations did not exceed the POR 75<sup>th</sup> percentile for all Southern Everglades downstream receiving water sampling locations during 2008 (see Appendix 3B-1).

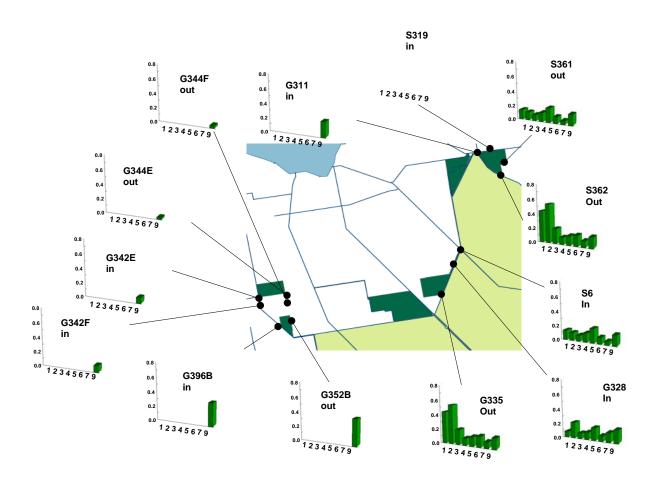
All fish species from the interior cells (ST1EC2A, ST1EC4SA, and ST1EC6A) of STA-1E show no visible temporal increase in THg levels for ≥ three years to merit statistical investigation.

Regarding risks to fish-eating wildlife, interior mosquitofish (falling under TL 2 or 3) did not exceed the USEPA's 77 ng/g criterion; however, the mosquitofish from the downstream location

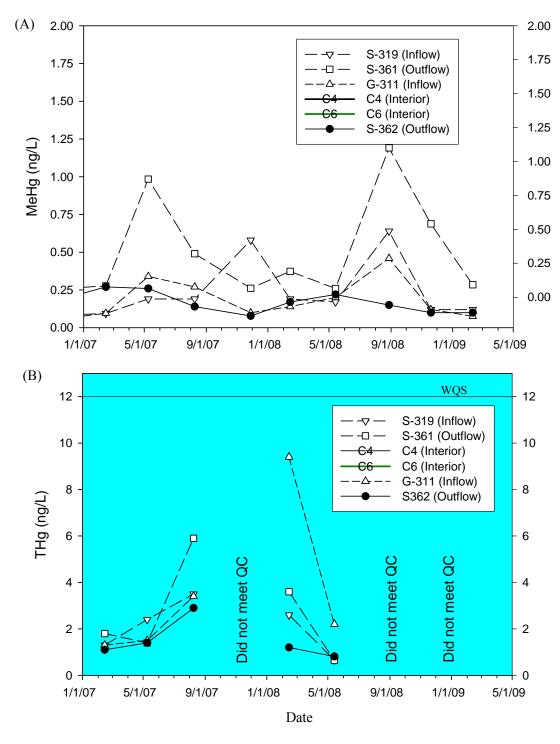
did exceed this criterion over all four quarters. Nearly all resident interior sunfish within STA-1E were well below the USFWS criterion of 100 ng/g and the USEPA predator protection criterion of 77 ng/g for TL 3 fish. Most of the exceedance for sunfish was due to the elevated concentrations from the downstream location ( $292 \pm 15$  ng/g). After standardizing by whole fish length concentration [fillet concentration x 0.695 (Lange et al., 1998)], there was no exceedance of the USEPA criterion of 346 ng/g for TL 4 fish species for LMB. Therefore, fish-eating wildlife foraging preferentially at STA-1E appear to have an overall low to moderate risk of mercury exposure.



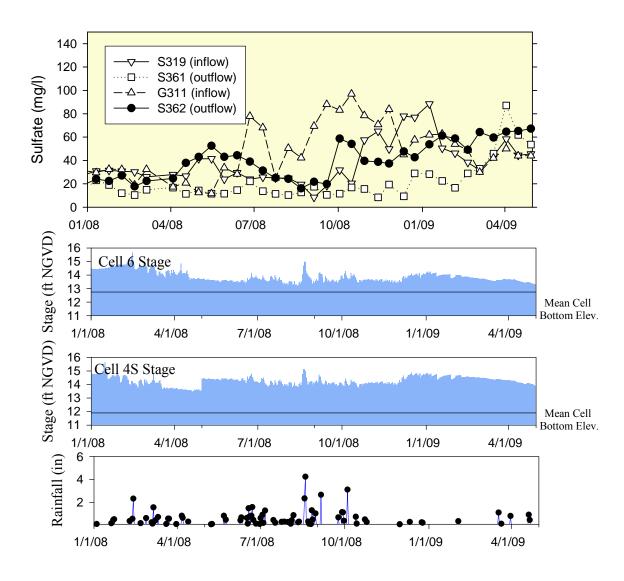
**Figure 10.** Annual median THg concentrations (ng/L) for all STAs during WY2009. Certain stations show only one year point due to their inclusion into surface water monitoring in WY2009.



**Figure 11.** Annual median MeHg concentrations (ng/L) for all STAs during the WY2009 period of record. Certain stations show only one year point due to their inclusion into surface water monitoring in WY2009.



**Figure 12.** Concentrations of (A) MeHg and (B) THg (ng/L) in unfiltered surface water collected at STA-1E.



**Figure 13.** Water-column sulfate, stage (recorded immediately upstream of outflow culvert of cell), and rainfall at STA-1E.

Table 6. THg and MeHg loadings for inflow and outflow for STAs during WY2009.

	Inflo	w load	Ouflo	w load	% Difference <sup>1</sup>	
	THg MeHg		THg	MeHg	THg	MeHg
STA-1E <sup>2,3</sup>	206	46	145	27.4	-30.0	-40.4
STA-2 <sup>4</sup>	160	65.3	234	60.6	46.0	-7.20
STA-5⁵		1.17	_	0.12		-89.7
STA-6 <sup>6</sup>	58.4	1.98	71.5	8.67	22.4	337

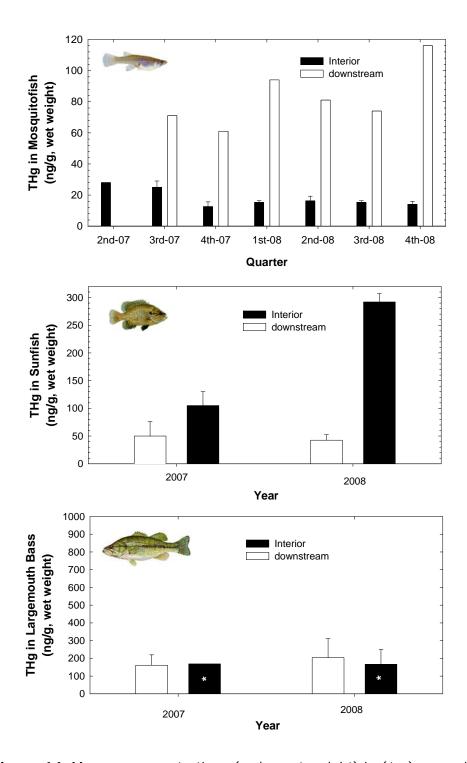
<sup>1 (</sup>outflow-inflow/inflow)\*100

<sup>&</sup>lt;sup>2</sup> Note: monitoring terminated in STA-3/4 and STA-1W; includes stations S319, S361, G311 (inflow), and S362 (outflow)

<sup>&</sup>lt;sup>4</sup> includes stations S6, G328 (inflow) and G335(outflow)

<sup>&</sup>lt;sup>5</sup> includes stations G342E, G342F (inflow, Flow-way 3) and G344E, G344F (outflow, Flow-way 3)

<sup>&</sup>lt;sup>6</sup> includes stations G600, G396B (inflow) and stations G354, G393, G354C, G393B, and G352B (outflow)



**Figure 14.** Mercury concentrations (ng/g, wet weight) in (*top*) mosquitofish composites ( $\pm$ SD), (*middle*) whole sunfish ( $\pm$ SD), and (*bottom*) fillets of largemouth bass (arithmetic, SD) collected at STA-1E. An asterisk indicates an arithmetic mean of all available largemouth bass.

#### STA-2

STA-2 Cells 2 and 3 met mercury start-up criteria in September 2000 and November 2000, respectively. In August 2001, flow-though operation of Cell 1 was approved under a permit modification. Cell 1 met start-up criteria in November 26, 2002. Operational monitoring of mercury at STA-2 began during the third quarter of 2001 after completion of the S-6 connection (Rumbold and Fink, 2002b, 2003b; Rumbold 2004, 2005a; Rumbold et al., 2006). The most recently developed Cell 4 passed mercury start-up criteria and flow-through began in 2007. Currently, all of STA-2 is under Phase 2 monitoring.

Results from monitoring mercury concentrations in surface water at STA-2 (**Figure 15**) show THg concentration in inflow and outflow did not exceed the Class III numerical water quality standard of 12 ng/L during WY2009. More importantly, both MeHg, which has no numerical WQS, and THg remained at low concentrations in the outflow despite a steady increase since 2005. Outflow load of MeHg was less than inflow and outflow load for THg was greater than inflow. The loading estimate for THg is highly uncertain as only one value was available to calculate loading for the entire water year as a result of QA/QC failures. It should also be noted that high outflow loading of THg may have resulted from the start-up of cell 4. During June 2008 water level stage fell below mean cell bottom elevation for approximately one month in Cell 1. This drop in water level had no visible impact on sulfate levels (**Figure 16**).

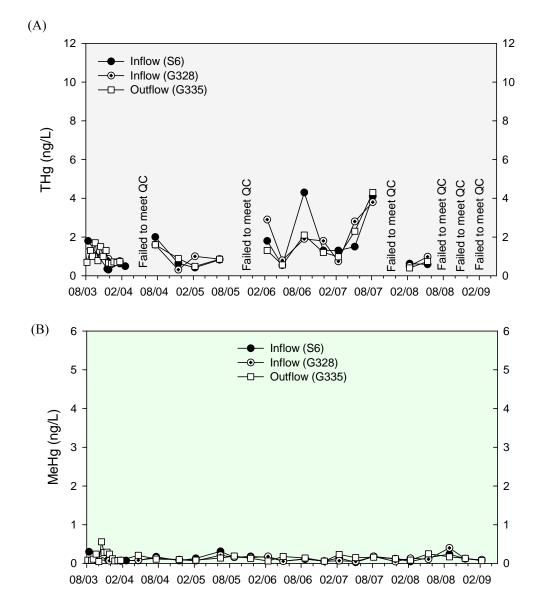
**Table 3** and **Figure 17** summarize results from operational monitoring of mercury concentrations in STA-2 mosquitofish for CY2008. **Figure 17** graphs results from different interior sites separately for this STA because of the degree of spatial variability previously observed. Starting in mid-2007, interior mosquitofish levels steadily increased until the second quarterly collection in 2008 then decreased thereafter. This rise and fall is likely related to the operational startup of Cell 4 in 2007. In 2008, the average mosquitofish composite and each individual mosquitofish composite for all STA-2 locations did not exceed the POR 75<sup>th</sup> percentile for all Southern Everglades sampling locations (see Appendix 3B-1).

Sunfish from STA-2 interior cells show no major change since 2007 (**Table 2** and **Figure 17**). As is expected, the newly established downstream site CA2NF shows considerably higher levels than the previously sampled outflow stations. Standardizing by species (bluegill) and length reveals the same general trend in concentration distribution between interior and downstream locations. Following standardization, average concentration was 0.36 ng/g/mm at interior locations and 0.88 ng/g/mm for the downstream location. In 2008, the average annual sunfish concentration for all STA-2 locations did not exceed the POR 75<sup>th</sup> percentile for all Southern Everglades sampling locations (see Appendix 3B-1).

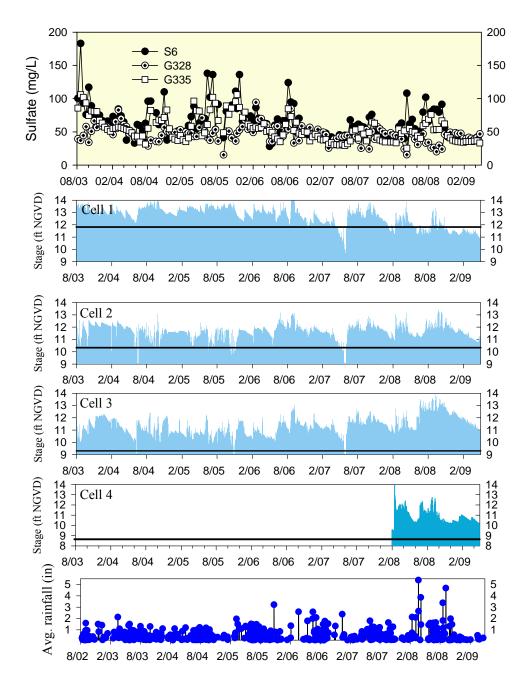
Concentrations of THg in fillets of resident largemouth bass from STA-2 (**Table 3** and **Figure 17**) between the length range of 280 to 330 mm reflect an overall average of  $255 \pm 57$  ng/g collected across Cell 4, which is the highest of all interior STA sites. Fish THg levels within this STA have consistently been on the high end in comparison all other STAs, which may be related to the previous non-cultivated land use within this area. Annual largemouth bass concentration for all STA-2 locations did not exceed the POR  $75^{th}$  percentile for all Southern Everglades downstream receiving water sampling locations (see Appendix 3B-1).

Mosquitofish and sunfish from the interior locations (STA2C1X and ST2C4A) of STA-2 showed no visible temporal increase for  $\geq$  three years. Largemouth bass do show a steady increase within Cell 4 (ST2C4A) for the past two years. Next year's temporal analysis will be used to determine if action is needed to help lower mercury levels in LMB within this cell.

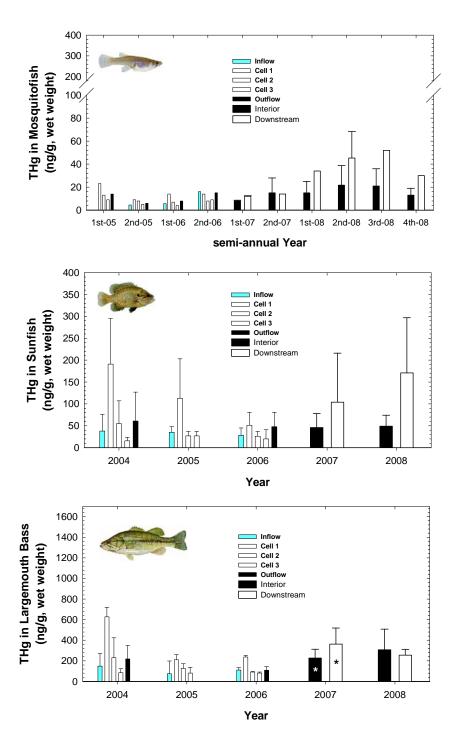
Regarding risk to fish-eating wildlife, in CY2008 no mosquitofish composite or sunfish within STA-2 contained mercury levels greater than the USEPA predator protector criteria of 77 ng/g for TL 2 or TL 3 species or the USFWS criteria of 100 ng/g. After standardizing by whole fish length concentration [fillet concentration x 0.695 (Lange et al., 1998)], there was no exceedance of the USEPA criterion of 346 ng/g for TL 4 fish species for LMB within STA-2. Overall, fish-eating wildlife foraging preferentially at STA-2 appear to have an overall moderate risk of mercury exposure.



**Figure 15.** Concentrations of (A) THg and (B) MeHg (ng/L) in unfiltered surface water collected at STA-2.



**Figure 16.** Water-column sulfate, stage (recorded immediately upstream of outflow culvert of cell), and rainfall totals at STA-2.



**Figure 17.** Mercury concentrations (ng/g, wet weight) in (*top*) mosquitofish composites (±SD), (*middle*) whole sunfish (±SD), and (*bottom*) fillets of largemouth bass (arithmetic, SD) collected at STA-2. An asterisk indicates an arithmetic mean of all available largemouth bass.

## STA-3/4

STA-3/4 Cell 1 satisfied start-up criteria for mercury in January 2004; the first discharges of treated water from this STA were in February 2004. Accordingly, routine operational monitoring of this flow-way began during the first quarter of 2004. STA-3/4, Cell 3, satisfied start-up criteria for mercury in June 2004 and Cell 2 passed in August 2004; with consensus from FDEP in September 2004, discharges began (for discussion of results observed prior to 2005, see Rumbold et al., 2006). In 2007, all mercury monitoring was moved into Phase 3 – Operational Monitoring (SFWMD, 2006). Thus, surface water monitoring for THg and MeHg was terminated. The last surface water dataset was collected in March 2008. Information on THg and MeHg for STA-3/4 is presented in previous SFERs.

Concentrations of THg in mosquitofish are summarized in **Table 1** and **Figure 18**. For CY2008, mosquitofish from STA-3/4 had low to moderate levels compared to all other STAs, which was the typical scenario in past years. There has been no major change in concentrations within STA-3/4 since 2006. In the past, this STA, along with STA-5, demonstrated the largest difference between inflow and outflow mosquitofish THg levels (e.g., 50 percent difference). This suggests that efficient MeHg bioaccumulation or food web exchange occurs within the STA-3/4 marsh since MeHg levels at the outflow of this STA are not significantly higher than other STAs. The average annual composite for CY2008 and each individual mosquitofish composite within STA-3/4 did not exceed the POR 75<sup>th</sup> percentile for POR for all receiving water sampling Everglades locations during the year (see Appendix 3B-1).

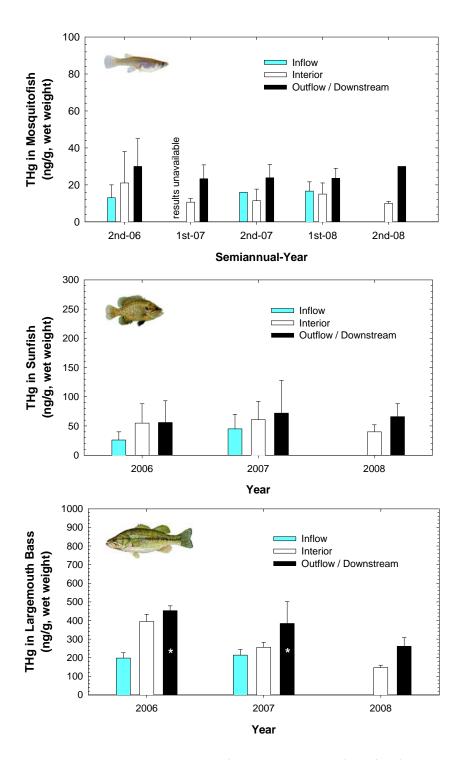
Similar to mosquitofish, resident sunfish from the interior marshes of STA-3/4 contained moderate mercury levels compared to fish from other STAs for CY2008 (**Table 2** and **Figure 18**). The average annual sunfish concentration within STA-3/4 did not exceed the POR 75<sup>th</sup> percentile for all Southern Everglades sampling locations (see Appendix 3B-1).

THg levels in LMB from STA-3/4 were in the moderate range (**Table 3**) similar to CY2007 and previous years. Since 2006, levels have demonstrated a steady decrease. The average annual LMB concentration for all locations within STA-3/4 did not exceed the POR 75<sup>th</sup> percentile for all Southern Everglades sampling locations during CY2008 (see Appendix 3B-1).

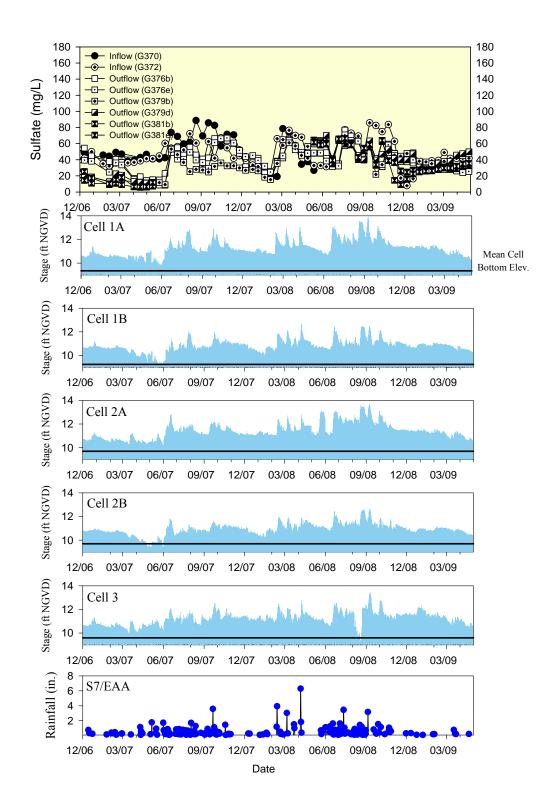
Annual average levels of each fish species within each interior location (STA34C1B1, STA34C2B4, and STA33) of STA-3/4 show no visible temporal increase for ≥ three years.

Regarding risk to fish-eating wildlife, mosquitofish from STA-3/4 contained mercury at concentrations lower than the USFWS (100 ng/g) and USEPA criterion (77 ng/g). Only one sunfish from the downstream location exceeded the USFWS criterion. After adjusting the arithmetic mean, mercury concentrations in fillets to whole-body concentrations (whole-body THg concentration = 0.69 x fillet THg; Lange et al., 1998) all largemouth bass from inflow, interior marshes, and outflow were less than the USEPA predator protection criteria based on TL 4 fish (346 ng/g). These results are a large improvement over last year. Therefore, fish-eating wildlife foraging preferentially at STA-3/4 appears to have an overall low to moderate risk of mercury exposure.

Water-column sulfate, stage, and rainfall at STA-3/4 are presented in **Figure 19**.



**Figure 18.** Mercury concentrations (ng/g, wet weight) in (*top*) mosquitofish composites (±SD), (*middle*) whole sunfish (±SD), and (*bottom*) fillets of largemouth bass (arithmetic, SD) collected at STA-3/4. An asterisk indicates an arithmetic mean of all available largemouth bass.



**Figure 19.** Water-column sulfate, stage (recorded immediately upstream of outflow culvert of cell), and rainfall at STA-3/4.

### STA-5

STA-5 met start-up criteria for mercury in September 1999. However, because of drought conditions and the detection of high phosphorus concentrations at the outflows, STA-5 did not begin flow-through operation until July 2000 (for discussion of results observed prior to 2005, see Rumbold and Rawlik, 2000; Rumbold et al., 2001 and 2006; Rumbold and Fink, 2002a and 2003a; Rumbold, 2004 and 2005a). The new section, Flow-way 3, is under Phase 2 monitoring and Flow-ways 1 and 2 are under Phase 3 monitoring.

As shown in **Figure 20**, water-column concentrations of MeHg in WY2008 remained low in STA-5. Information on surface water THg is not displayed as all data were qualified during the available sampling periods. On January 1, 2009, surface water sampling was temporally suspended due to dryout conditions. The consistent dry-out rewet patterns have created elevated surface water sulfate concentrations (**Figure 21**). Regarding THg and MeHg loading, outflow loading of MeHg was less than inflow for. Loading could not be calculated for THg as all surface water samples failed QA/QC criteria during WY2009 (**Table 6**).

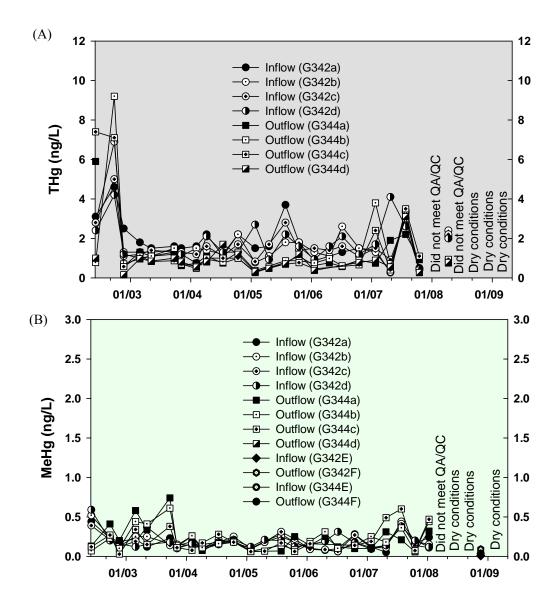
Mosquitofish collected from STA-5 in CY2008 contained moderate to high mercury levels (**Figure 22**), compared to all other STAs (**Table 1**). Average levels for CY2008 in the interior marsh were nearly double levels in 2007. The high THg levels at the peak of the parabolic trend in 2008 are attributed to startup operations for Flow-way 3. This same trend occurred for mosquitofish in STA-2 which is likely related to start-up of Cell 4. These data suggest it requires approximately a full calendar year for fish THg levels to revert back to pre-startup conditions once an adjacent cell is brought into operation. This time for the reversion may not be uniform and could vary depending upon cell size, hydraulic connection to the cell brought online and physicochemical properties of the cell/operating unit(s). Mosquitofish from downstream collection sites were, as with all other STAs, higher than the interior marsh. The average annual mosquitofish composite for 2008 and each individual mosquitofish composite for all locations within STA-5 did not exceed the POR 75<sup>th</sup> percentile for all Southern Everglades sampling locations during 2008 (see Appendix 3B-1).

Similar to mosquitofish, sunfish collected from the interior marsh contained moderate mercury levels compared to STAs (**Table 2**). All but one sunfish were bluegill, therefore appropriate comparisons can be made to other STAs without standardizing by fish type. A rise in bluegill concentrations, as observed with mosquitofish, was not present. The average annual sunfish THg concentration for CY2008 within STA-5 did not exceed the POR 75<sup>th</sup> percentile for all Southern Everglades sampling locations (see Appendix 3B-1).

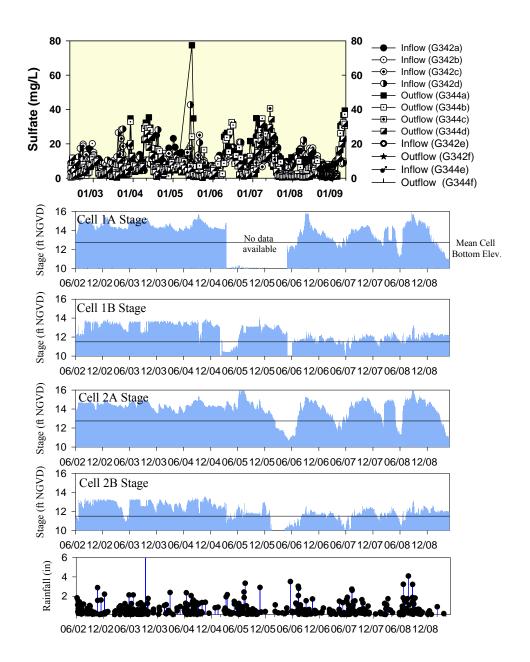
As in previous years, the Florida Fish and Wildlife Conservation Commission (under contract to the District to electroshock and collect large-bodied fish for mercury monitoring) encountered difficulties in filling sample quotas for STA-5. In spite of the difficulties with fish collection, a start-up-associated increase in mercury was not observed for LMB, revealing the level of bioaccumulation disconnect between large and small-bodied fish. For CY2008, no LMB were collected from the downstream site RA1 (**Table 3**). The lack of fish collection and inability to age-standardize has made long-term evaluation of LMB in this STA difficult. However, there does appear to be a decline in mercury concentrations since sample collection began in 1999 (**Figure 22**). The average annual LMB THg concentration collected in STA-5 did not exceed the POR 75<sup>th</sup> percentile for all Southern Everglades sampling locations.

Annual average mercury levels in each fish species within the marsh sites (STA5C1B1, STA5C2B1, and STA5C3B1) of STA-5 show no visible temporal increase for  $\geq$  three years.

Regarding the risk to fish-eating wildlife, all resident mosquitofish and sunfish, except one, within the marsh of STA-5 contained mercury levels below the USEPA criterion of 77 ng/g for TL 3 fish species and the USFWS criterion of 100 ng/g. Largemouth bass from the interior marsh of STA-5 were all below the USEPA criterion of 346 ng/g for TL fish species [fillet concentration x 0.695 (Lange et al., 1998)]. Therefore, fish-eating wildlife foraging preferentially from the interior marsh of STA-5 appears to be at moderate risk from mercury exposure and at a slight elevated risk if feeding near site RA1.



**Figure 20.** Concentrations of (A) THg and (B) MeHg (ng/L) in unfiltered surface water collected at STA-5.



**Figure 21.** Concentrations of sulfate (*top*), stage in the two cells (recorded immediately upstream of outflow culvert of cell), and rainfall at STA-5.

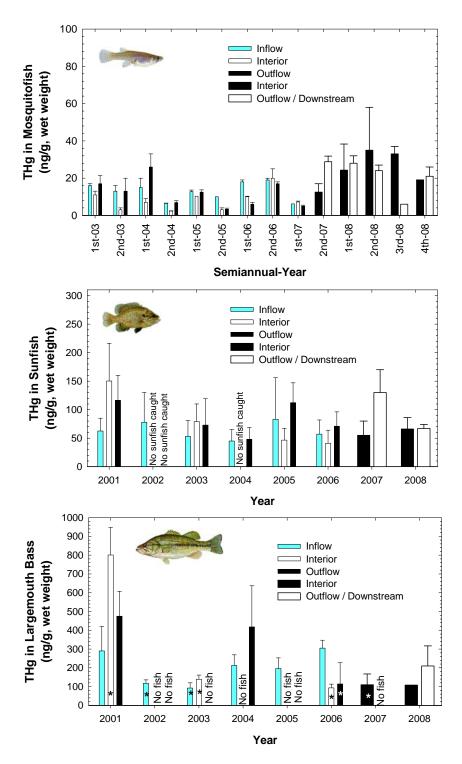


Figure 22. Mercury concentrations (ng/g, wet weight) in (top) mosquitofish composites ( $\pm$ SD), (middle) whole sunfish ( $\pm$ SD), and (bottom) fillets of largemouth bass (arithmetic, SD) collected at STA-5. An asterisk indicates an arithmetic mean of all available largemouth bass.

### STA-6

STA-6, Section 1 (Cells 3 and 5) met start-up criteria for mercury in November 1997, and began operation in December 1997. Routine monitoring of mercury at STA-6 was initiated in the first calendar quarter of 1998. Monitoring results prior to May 2004 have been reported (SFWMD, 1998c and 1999d; Rumbold and Rawlik, 2000; Rumbold et al., 2001; Rumbold and Fink, 2002a; Rumbold and Fink, 2003a; Rumbold, 2004 and 2005a; Rumbold et al., 2006). Start-up mercury monitoring occurred in the new section of STA-6, Section 2, on July 25, 2007. Currently, all of STA-6 is under Phase 2 monitoring.

THg concentrations at the inflows and outflows were consistent throughout WY2009 (**Figure 23**) and remained relatively low compared to previous spikes. MeHg remained at very low concentrations throughout the year as well. However, as shown in **Figure 24**, both cells dried down during WY2009 for two periods lasting approximately three months each. These dryout periods likely resulted in the high surface water sulfate levels observed in STA-5. The relatively low concentrations of both THg and MeHg in the outflows appear incongruous with hypotheses previously offered regarding dryout and rewetting effects on sediment oxidation, sulfur biogeochemistry, and stimulation of methylation by sulfate-reducing bacteria (Rumbold et al., 2006). Nonetheless, it is reasonable to assume that the dryout and rewetting of this rain-driven STA has some part in higher tissue-Hg levels in large-bodied fish. For WY2009, outflow loading of THg and MeHg were both greater than inflow; however, there estimates are highly uncertain due the lack of data that resulted from QA/QC failures during WY2009. Accurate loading evaluation is further confounded by the start-up of section 2 during 2008 which could have produced temporary high outflow loading of THg and MeHg (**Table 6**).

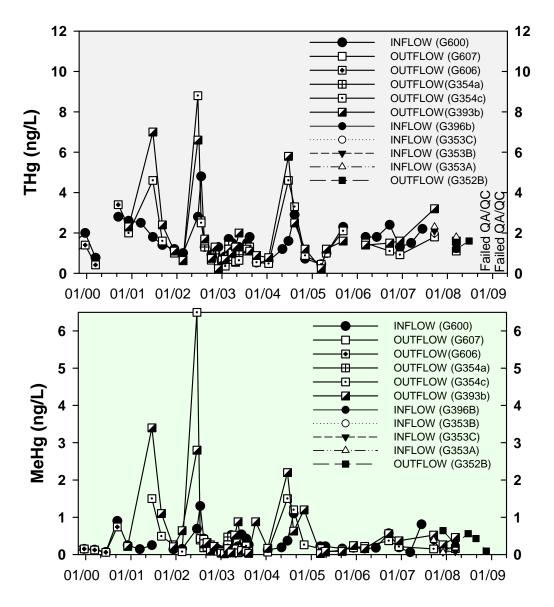
Concentrations of THg in mosquitofish are summarized in **Table 1** and graphically presented in **Figure 25**. Levels of mercury in mosquitofish from the interior of STA-6 for CY2008 were uncharacteristically high compared to past years. This large increase is likely related to the start-up of Section 2 in 2008. An increase in fish THg without an observed similar increase in surface water MeHg may indicate changes in food chain dynamics that enhanced mercury bioaccumulation. However, this does not consider potential changes in porewater MeHg. The average annual composite for 2008 and each individual mosquitofish composite for all locations within STA-6 did not exceed the POR 75<sup>th</sup> percentile for all Southern Everglades sampling locations (see Appendix 3B-1).

As shown in **Table 2** and **Figure 25**, STA-6 sunfish from the interior marsh for CY2008 had mercury levels greater than those observed in sunfish at all other STAs, with the exception of locations within the Everglades and EPA downstream monitoring locations. This has been the scenario since STA-6 was put into operation. The average annual sunfish Hg concentration for the interior marsh of STA-6 did not exceed the 75<sup>th</sup> percentile for POR for all receiving waters sampled in Southern Everglades locations during 2008 (see Appendix 3B-1).

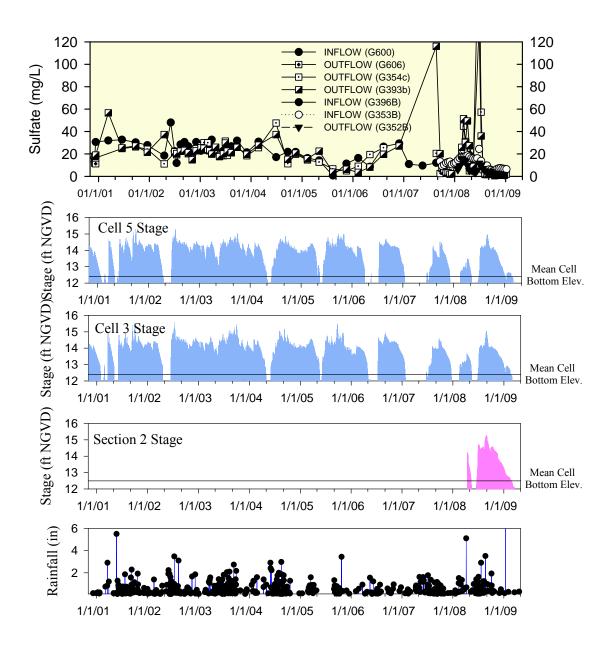
Largemouth bass at the interior site (STA6S2) had much lower concentrations compared to 2007 (50 percent decrease) (**Figure 25**); however, this decrease should be viewed with caution as the arithmetic mean was comparable to last year due to the inability to standardize fish by age three. The downstream site (STA6DC) had much higher levels than the interior, 252 ng/g versus 386 ng/g downstream. Although highly variable, the interior concentrations still show a decreasing trend since the start of the POR. The average annual LMB collected for 2008 in STA-6 did not exceed the POR 75<sup>th</sup> percentile for all Southern Everglades sampling locations.

Annual average mercury levels in each fish species within the marsh sites (STA6S2, STA6C52, and STA6C32) of STA-6 show no visible temporal increase for  $\geq$  three years.

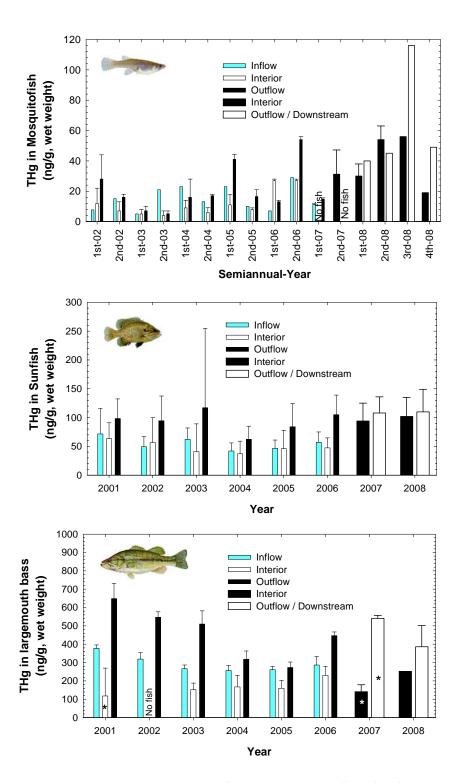
Regarding risks to fish-eating wildlife, mosquitofish from the interior and downstream locations did not exceed the 77 ng/g TL 3 USEPA criterion except for one downstream sample in 2008. For sunfish, however, 40 percent of the catch from the interior marsh exceeded the USEPA TL 3 criterion. All sunfish from the downstream site and nearly all from the interior marsh exceeded the USFWS criterion. All largemouth bass (whole-body concentration estimated from fillet concentration) from the interior marsh of STA-6 were above the USFWS criterion, (100 ng/g) but none were above the USEPA criterion of TL 4 species (346 ng/g). For the downstream location of STA-6, all LMB exceeded the USFWS criterion and one fish sample exceeded the USEPA TL 4 criterion. Therefore, the risk of mercury exposure to fish-eating wildlife foraging preferentially at interior and downstream locations within STA-6 appears to be moderate to elevated.



**Figure 23.** Concentrations of (A) THg and (B) MeHg (ng/L) in unfiltered surface water collected at STA-6.



**Figure 24.** Concentrations of sulfate (*top*), stage in the two cells (recorded immediately upstream of outflow culvert of cell), and rainfall at STA-6.



**Figure 25.** Mercury concentrations (ng/g, wet weight) in (top) mosquitofish composites ( $\pm$ SD), (middle) whole sunfish ( $\pm$ SD), and (bottom) fillets of largemouth bass (arithmetic, SD) collected at STA-6. An asterisk indicates an arithmetic mean of all available largemouth bass.

# OPTIMIZING THE MERCURY MONITORING NETWORK

A key component of any monitoring program is periodic reevaluation of objectives and methods to more sharply focus available finite resources. The monitoring plan should be revisited regularly to determine if improvements — such as using a different data collection method or a revised sampling regime — can be implemented without compromising the quality of the data stream while continuing to meet the program's objectives. In early 2005, a strategic plan was drafted to optimize the District's Mercury Monitoring Plan (Rumbold, 2005b). This strategic plan was approved and the formalized into the Protocol (SFWMD, 2006) (see the *Summary of the Mercury Monitoring and Assessment Program* section of this appendix). The summaries below provide information on ways in which mercury monitoring has been optimized for each STA to date which are concurrent which guidance contained in the Protocol.

### STA-1W/STA-1E

The most recent STA-1W/STA-1E EFA permit was issued on November 6, 2007. The mercury monitoring requirements contained under Section 4 of Downstream Receiving Water Monitoring for the EFA STA permit were omitted during the renewal process and instead codified in the non-EFA structures permit upon renewal. STA-1E is under Phase 2, Tier 1 and STA-1W is under Phase 3, Tier 1.

STA-1W mosquitofish are collected in one composite sample per flow-way (ST1W13COM, ST1WC24COM, and ST1WC5COM) and a single sample from a new downstream station (ST1WLX) located in the Arthur R. Marshall Loxahatchee National Wildlife Refuge are collected semiannually. Mosquitofish were monitored at the downstream station, ST1WLX and monitoring was discontinued at G310 and ENR012. In the fall 2009, the District expects to request moving all mercury monitoring in STA-1W into Phase 3-Tier3.

Consistent with the Protocol, annual LMB and sunfish monitoring frequency was reduced from annually to triennially and was reduced to one flow-way and one downstream station. The n=20 requirement was reduced to n=5 at each station, and LMB ageing is no longer required (since a more specific size range is targeted). Largemouth bass and sunfish monitoring was discontinued at stations S5A, ENR302, and ENR401; instead, these fish will be collected from the flow-way with the highest observed concentrations at Cell 5 (ST1W51). In addition, LMB was monitored at the downstream station, ST1WLX and monitoring was discontinued at G310 and ENR012.

## STA-2

The most recent STA-2 EFA permit was issued on September 4, 2007. The mercury monitoring requirements contained under Section 4 of Downstream Receiving Water Monitoring for the EFA STA permit were omitted during the renewal process and instead codified in the non-EFA structures permit upon renewal. Mercury monitoring in STA-2 is currently under Tier 2 monitoring.

STA-2 mosquitofish were collected quarterly as one composite sample per flow-way (ST2C1COM, ST2C2COM, ST2C3COM, and ST2C4COM) and as a single sample from a downstream station (CA2NF). CA2NF has been monitored since 2005 for the non-EFA permit as an alternate to station N4. Three years of data were available to compare G335 and CA2NF for spatial variability. In 2009, this analysis was performed and results indicated no spatial variability existed between these two stations, therefore all fish monitoring at station G335 was dropped.

Annual LMB and sunfish monitoring was reduced to one flow-way and one downstream station. In addition, consistent with the Protocol (SFWMD, 2006), n = 20 was reduced to n = 5 for LMB and sunfish at each station and specific size ranges are targeted instead of ageing (102 to 178 mm for bluegill and 280 to 330 for mm LMB). LMB and sunfish monitoring was discontinued at stations G328B, STA2C2A, STA2C3A, and G335. Bass and sunfish will continue to be collected from the flow-way with the highest observed concentrations, Cell 1 (STA2C1X) and from the downstream station CA2NF.

## STA-3/4

The most recent STA-3/4 permit modification was issued on September 4, 2007. The mercury monitoring requirements contained under Section 4 of Downstream Receiving Water Monitoring for the EFA STA permit were omitted during the renewal process and instead codified in the non-EFA structures permit upon renewal. All of STA-3/4 is currently under Phase 3, Tier 1 monitoring.

STA-3/4 mosquitofish were quarterly as one composite sample per flow-way (ST34C1COM, ST34C2COM, and ST34C3COM) and along the discharge canal (L5F1).

LMB and sunfish monitoring frequency was reduced from annually to triennially and monitoring locations to one flow-way and one downstream station. These fish will continue to be collected from the flow-way with the highest observed concentrations, Cell 3 (ST34C33) and from the downstream station, L5F1. Consistent with the Protocol, LMB and sunfish collections were reduced from n = 20 to n = 5 at each station and a specific size range of fish was targeted.

In addition to the fish sampling changes, surface water sampling for THg analysis was dropped at G370, G372, G376B, G376E, G379B, G379D, G381B, and G381E due to EFA modifications. Sediment collection for THg analysis was dropped from STA-3/4 on May 16, 2008.

### STA-5

The new STA-5 EFA permit was issued September 4, 2007 and permit modification was issued May 16, 2008. The mercury monitoring requirements contained under Section 4 of Downstream Receiving Water Monitoring for the EFA STA permit were omitted during the renewal process and instead codified in the non-EFA structures permit upon renewal. Currently, Hg monitoring occurs in Flow-ways 1 and 2. The new section, Flow-ways 3, is under Phase 2 monitoring and Flow-ways 1 and 2 are under Phase 3 monitoring.

STA-5 mosquitofish are collected quarterly as one composite sample per flow-way (ST5C1COM, ST5C2COM, and ST5C3COM) and as a single sample from a downstream station RA1 in the Rotenberger Wildlife Management Area. Discharge stations G344B and G344D and downstream station RA1 were sampled in 2008. If no spatial variability exists between RA1 and G334B and G334D, then monitoring will be terminated at G344B and G344D.

Annual bass and sunfish monitoring was reduced to Flow-ways 2 and 3 and one downstream station. Bass and sunfish monitoring was discontinued at the Flow-way 1 and 2 inflow station (G342A), Flow-way 2 interior station (STA5C2B1) and Flow-way 1 and 2 discharge stations (G344B and G344D). LMB and sunfish will continue to be collected from the interior of the flow-way with the highest observed concentrations, Cell 1 (ST5C1B1) and from the downstream station RA1. Discharge stations G344B and G344D and downstream station RA1 were sampled in 2008. If no spatial variability exists between G344B and G344D and RA1, monitoring will be terminated at G344B and G344D. Consistent with the Protocol, LMB and sunfish collections were reduced from n = 20 to n = 5 at each station and ageing was eliminated since a specific size range is targeted.

In addition to fish sampling, on May 16, 2008, surface water sampling for THg analysis was dropped at G342A–D and G344A–D.

## STA-6

The most recent STA-6 EFA permit was issued on September 4, 2007 and a permit modification was issued on May 16, 2008. The mercury monitoring requirements contained under Section 4 of Downstream Receiving Water Monitoring for the EFA STA permit were omitted during the renewal process and instead codified in the non-EFA structures permit upon renewal. The new STA-6 section, Section 2, is under Phase 2 monitoring. All mercury monitoring was terminated in Section 1 on June 6, 2008, consistent with Phase 3, Tier 3 monitoring.

Mosquitofish are collected quarterly as one flow-way composite for Section 2 (STA6COM) and a STA-6 downstream station (STA6S2).

Annual LMB and sunfish monitoring was eliminated at the inflow (G600), Cell 3 interior (STA6C32) and discharge (G393B), and Cell 5 interior (STA6C52) and discharge (G354C). Bass and sunfish monitoring are required only for the STA-6 Section 2 interior (STA6S2) and the STA-6 downstream station STA6S2. Consistent with the Protocol, LMB and sunfish collections were reduced from n = 20 to n = 5 at each station and ageing was eliminated since a specific size range is targeted.

In addition to fish sampling on June 6, 2008, surface water sampling for THg analysis was dropped at G353A–C, G354C, and G393B.

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## **Attachment:**

## SOIL-62 Final Report: Soil/Hazardous Waste Proficiency Testing

Note: For reader convenience, this attachment is being reproduced verbatim and has not been revised through peer review or by the SFER production staff. This appendix was provided by Environmental Resource Associates, Arvada, CO, for the South Florida Water Management District.

Zdzislaw Kolasinski South Florida Water Mgt Dist Water Quality Analysis Div 1480 Skees Rd Bldg #9 West Palm Beach, FL 33411



## **Soil/Hazardous Waste Proficiency Testing**

**Soil Study** 

Open Date: 04/21/08

Close Date: 06/05/08

Report Issued Date: 06/26/08

June 25, 2008

Zdzislaw Kolasinski South Florida Water Mgt Dist Water Quality Analysis Div 1480 Skees Rd Bldg #9 West Palm Beach, FL 33411

Enclosed is your final report for ERA's SOIL-62 Proficiency Testing (PT) study. Your final report includes an evaluation of all results submitted by your laboratory to ERA.

Data Evaluation Protocols: All analytes in ERA's SOIL-62 Proficiency Testing (PT) study have been evaluated using the following tiered approach. If the analyte is listed in the most current National Environmental Laboratory Accreditation Conference (NELAC) PT Field of Testing tables, the evaluation was completed by comparing the reported result to the acceptance limits generated using the criteria contained in the NELAC FoPT tables. If the analyte is not included in the NELAC FoPT tables, the reported result has been evaluated using the procedures outlined in ERA's Standard Operating Procedure for the Generation of Performance Acceptance Limits (SOP 0260).

Corrective Action Help: As part of your accreditation(s), you may be required to identify the root cause of any "Not Acceptable" results, implement the necessary corrective actions, and then satisfy your PT requirements by participating in a Supplemental (QuiK™ Response) or future ERA PT study. ERA's technical staff is available to help your laboratory resolve any technical issues that may be impairing your PT performance and possibly affecting your routine data quality. Our laboratory and technical staff have well over three hundred years of collective experience in performing the full range of environmental analyses. As part of our technical support, ERA offers QC samples that can be helpful in helping you work through your technical issues.

Thank you for your participation in ERA's SOIL-62 Proficiency Testing study. If you have any questions, please contact Shawn Kassner, Proficiency Testing Manager, or Curtis Wood, Quality Assurance Director, at 1-800-372-0122.

Sincerely,

Shawn Kassner Proficiency Testing Manager

Shawn Kassmer

Curtis J. Wood Quality Assurance Director

whighout

attachments smk

Report Recipient	Report Recipient Contact/Phone Number	
Florida	Steve Arms / 904-791-1502	All Analytes

## SOIL-62 Definitions & Study Discussion

Study Dates: 04/21/08 - 06/05/08 Report Issued: 06/26/08

#### **SOIL Study Definitions**

The Reported Value is the value that the laboratory reported to ERA.

The ERA assigned value for the Organic Proficiency Testing Standards is equal to 100% of the parameter present in the standard as determined by gravimetric and/or volumetric measurements made during standard preparation as applicable. The ERA assigned value for the Inorganic Proficiency Testing Standards, with the exception of the TCLP Metals in Soil, is equal to the maximum amount of the parameter available in the standard by applicable EPA methodologies. The ERA assigned value for the TCLP metals is equal to the mean of ERA's internal analytical analyses. All NELAC parameters not added to a standard are given an assigned Value of "0", per the guidance issued by the NELAC Board of Directors, on December 14, 2000. Non-NELAC parameters not added to a standard may be given an assigned value of less than a minimum verified concentration as determined in the background soil for applicable EPA methodologies.

The Acceptance Limits are established per the criteria contained in the most current USEPA/NELAC FoPT tables, or ERA's SOP for the Generation of Performance Acceptance Limits™ as applicable.

The Performance Evaluation:

Acceptable = Reported Value falls within the

Acceptance Limits.

Not Acceptable = Reported Value falls outside the

Acceptance Limits.

No Evaluation = Reported Value cannot be evaluated.

Not Reported = No Value reported.

The Method Description is the method the laboratory reported to ERA.

### **SOIL Study Discussion**

ERA's SOIL-62 Proficiency Testing (PT) study has been reviewed by ERA Senior Management and certified compliant with the criteria contained in the most current NELAC FoPT tables.

Per the requirements of the NELAC Proficiency Testing Program, a full review of all homogeneity, stability, and accuracy verification data was completed. All analytical verification data for all analytes in the study standards met the acceptance criteria contained in the most current NELAC FoPT tables.

The data submitted by participating laboratories was also examined for study anomalies. There were no anomalies observed during the statistical review of the data.

ERA's SOIL-62 Proficiency Testing study reports shall not be reproduced except in their entirety and not without the permission of the participating laboratories. The report must not be used by the participating laboratories to claim product endorsement by any agency of the U. S. government.

The data contained herein are confidential and intended for your use only.

If you have any questions regarding ERA's SOIL Proficiency Testing program, please contact Shawn Kassner, Proficiency Testing Manager, or Curtis Wood, Quality Assurance Director, at 1-800-372-0122.





Study: SOIL-62

ERA Customer Number: **S421405** 

Laboratory Name: South Florida Water Mgt

**Dist** 

# Inorganic Results





## SOIL-62 Final Complete Report

Zdzislaw Kolasinski Sr Scientist South Florida Water Mgt Dist Water Quality Analysis Div 1480 Skees Rd Bldg #9 West Palm Beach, FL 33411 561-681-2500 EPA ID: FL00103
ERA Customer Number: S421405
Report Issued: 06/26/08
Study Dates: 04/21/08 - 06/05/08

Anal. No.	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
SOIL N	letals in Soil						
1000	Aluminum	mg/kg		12100	4840 - 16200	Not Reported	
1005	Antimony	mg/kg		216	21.6 - 238	Not Reported	
1010	Arsenic	mg/kg		113	72.5 - 136	Not Reported	
1015	Barium	mg/kg	[	206	145 - 250	Not Reported	
1020	Beryllium	mg/kg		85.7	57.4 - 97.7	Not Reported	
1025	Boron	mg/kg		166	89.6 - 192	Not Reported	
1030	Cadmium	mg/kg		67.2	44.5 - 77.1	Not Reported	
1035	Calcium	mg/kg		10300	7440 - 12300	Not Reported	
1040	Chromium	mg/kg		262	167 - 305	Not Reported	
1050	Cobalt	mg/kg		103	67.9 - 115	Not Reported	
1055	Copper	mg/kg		189	131 - 216	Not Reported	
1070	Iron	mg/kg		18700	7570 - 28500	Not Reported	
1075	Lead	mg/kg		97.0	60.0 - 112	Not Reported	
1085	Magnesium	mg/kg		4220	2780 - 5230	Not Reported	
1090	Manganese	mg/kg		571	432 - 684	Not Reported	
1095	Mercury	mg/kg	8.92	8.69	4.34 - 12.6	Acceptable	EPA 7473
1100	Molybdenum	mg/kg		57.8	32.2 - 65.0	Not Reported	
1105	Nickel	mg/kg		152	98.1 - 170	Not Reported	
1125	Potassium	mg/kg		4900	2810 - 5790	Not Reported	
1140	Selenium	mg/kg		317	199 - 373	Not Reported	
1150	Silver	mg/kg		32.3	19.6 - 40.6	Not Reported	
1155	Sodium	mg/kg		1070	614 - 1420	Not Reported	
1160	Strontium	mg/kg		243	161 - 294	Not Reported	
1165	Thallium	mg/kg		139	82.1 - 161	Not Reported	
1175	Tin	mg/kg		115	59.4 - 148	Not Reported	
1180	Titanium	mg/kg		523	80.2 - 844	Not Reported	
1185	Vanadium	mg/kg		133	77.8 - 152	Not Reported	
1190	Zinc	mg/kg	[	647	437 - 753	Not Reported	

